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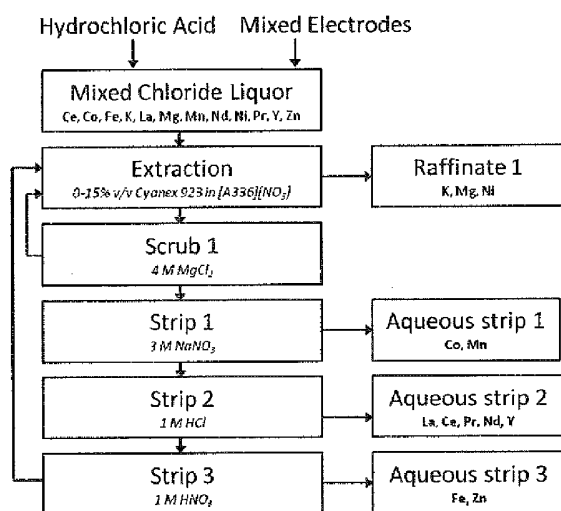


Figure 8.

(57) Abstract: The present invention relates to a new solvent extraction process for the extraction of rare earths as a group and for the separation of a mixture of rare earths into the individual elements. The rare earths are extracted from a feed solution containing anions that form weakly extracting complexes such as chloride or sulfate salts to an organic phase through complex formation with anions present exclusively in the organic phase. The organic phase comprises a water-immiscible ionic liquid with nitrate or thiocyanate anions. In addition to the ionic liquid, the organic phase can also contain a neutral extractant. The rare earths can easily be stripped as chloride or sulfate salts from the loaded organic phase.

## PROCESS FOR EXTRACTION AND SEPARATION OF RARE EARTHS BY SPLIT-ANION EXTRACTION WITH IONIC LIQUIDS

### FIELD OF THE INVENTION

The present invention relates to a new solvent extraction process for the extraction of rare earths as a group and for the separation of a mixture of rare earths into the individual elements. The rare earths are extracted from an aqueous feed solution containing anions that form weakly extracting complexes such as chloride or sulfate salts to an organic phase through complex formation with anions present almost exclusively in the organic phase. The rare earths can easily be stripped in chloride or sulfate form from the loaded organic phase.

### BACKGROUND OF THE INVENTION

The *rare earths* or *rare-earth elements (REEs)* are a group of 17 elements in the periodic system, consisting of scandium (Sc), yttrium (Y), lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb) and lutetium (Lu). The *lanthanides* are the series of elements from lanthanum to lutetium. The rare earths are also divided into the light rare-earth elements (LREEs) and the heavy rare-earth elements (HREEs). The LREEs correspond to the first half of the lanthanide series (i.e. La-Gd) and the HREEs to the second half (i.e. Tb-Lu). In rare-earth ores, yttrium accompanies the HREEs. Although scandium is defined as one of the REEs, its chemical properties are quite different from that of the other REEs. Scandium does not belong to either the LREEs or HREEs. Mixtures of rare earths are very difficult to separate into the individual elements, due to their very similar chemical properties. This is a major problem because rare earths occur in nature as mixtures, and many technological applications rely on the incorporation of rare-earth compounds with a high purity. For instance, the purity of europium and yttrium in the  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  red lamp phosphor is often as high as 99.999% (5N). The separation techniques used until the middle of the 20<sup>th</sup> century were classical methods such as fractional crystallization, fractional precipitation and selective oxidation or reduction. Since the 1950s, modern separation methods such as ion exchange, solvent extraction and extraction chromatography have been further developed to obtain rare-earth compounds in high purity. To date, *solvent extraction (SX)* is the most important separation technique for rare earths on an industrial scale. The separation of rare earths by solvent extraction depends upon the preferential distribution of rare-earth complexes

between two immiscible phases, typically an aqueous phase and an organic phase that are in contact with each other. *Extractants* (*extracting agents*) are used to transfer the rare earth from the aqueous to the organic phase. The most often used extractants for the separation of rare earths are: (1) *acidic extractants*, such as the phosphorus-containing extractants bis(2-ethylhexyl)phosphoric acid (HDEHP, D2EHPA or P204), (2-ethylhexyl)phosphonic acid, mono(2-ethylhexyl) ester (HEHEHP, or P507) and bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex 272), as well as carboxylic acids such as neodecanoic acid (Versatic Acid 10) and naphthenic acids; (2) *basic extractants* or *anion exchangers* such as quaternary ammonium salts (e.g. Aliquat 336); and (3) *neutral extractants* or *solvating extractants*, such as tri-*n*-butylphosphate (TBP), Cyanex 923 or Cyanex 925. Cyanex 923 is a mixture of 60% tri(*n*-hexyl)phosphine oxide and 40% tri(*n*-octyl)phosphine oxide. Cyanex 925 is a mixture of 85% bis(2,4,4-trimethylpentyl) *n*-octylphosphine oxide and 15% tris(2,4,4-trimethylpentyl)phosphine oxide. The separation of a complex mixture of rare earths is achieved via a *multistage counter-current extraction process*, using *mixer-settlers* to mix and separate the aqueous and organic phases. Typically, about 100 mixer-settlers are combined into a *cascade* or *battery* for each separation. Large rare-earth separation plants use more than 1000 extraction steps to separate a mixture of 15 rare earths into the individual elements.

The most often used extractants for the separation of rare earths on an industrial scale are the phosphorus-containing acidic extractants such as HDEHP, HEHEHP and Cyanex 272 (US Patent 4,647,438, US Patent 5,622,679). An advantage of these extractants is that one single extractant can be used for the separation of a mixture containing all the rare earths, thanks to the relatively large separation factors for neighbouring rare-earth ions. Another advantage is that they are widely applicable and that they can be used to extract rare-earth ions from aqueous feed solutions containing different types of anions (chloride, nitrate, sulphate, perchlorate), as long as the rare-earth ions are present in the aqueous feed solution as hydrated cations or cationic complexes. However, the acidic extractants have several disadvantages. The extraction process is pH-sensitive. Although selectivity can be achieved by pH control, adjustment of the pH requires a careful process control. Back-extraction (stripping) of the rare-earth ions from the loaded organic phase can be very difficult, due to the strong affinity of the rare-earth ions and especially of the heavy rare-earth ions (HREEs) for the acidic extractants. For instance, concentrated sulphuric acid or even hydrogen fluoride solutions are required to strip the heavy rare earths from the organic phase after extraction with HDEHP. The pH control and back-extraction consume considerable amounts of chemicals, both acids and bases. Acids are required for the pH control and back-extraction, bases are required for the pH control, for the pre-neutralization (saponification) of the acidic extractants before extraction and for neutralization of the very acidic stripping solutions.

As a consequence of the reactions between acids and bases, large amounts of salt waste are produced. Another disadvantage of acidic extractants is that it is impossible to work with very concentrated aqueous feed solutions. In general the concentrations of the aqueous feed solutions are between 30 and 50 g/L (total rare-earth oxide content). A high loading of the organic phase has to be avoided, because otherwise gel formation will occur and separation of the organic and aqueous phase will be no longer possible. In the case of HDEHP, gel formation will occur at approximately 50% saturation of the extractant (US Patent 4,016,237). The low rare-earth concentration in the aqueous feed solution results in low concentrations in the organic phase and in diluted aqueous solutions after back-extraction. The back-extraction solution is even further diluted by the large amounts of acids used for back-extraction. This leads to a low efficiency of the solvent extraction process. Moreover, the acids used for back-extraction can lead to contamination of the separated rare earths.

Neutral extractants offer several advantages over acidic extractants (US Patent 5,192,443). First of all, they can be used to extract rare earths from very concentrated aqueous feed solutions, containing 100 to 500 g/L of dissolved rare-earth oxides. This results in concentrated organic phases after extraction. There is less danger for gel formation in the highly loaded organic phases compared to extraction with acidic extractants. Secondly, the extraction process shows little dependence on the pH, so that careful pH control is not required. Thirdly, back-extraction can simply be achieved with neutral or slightly acidified water. The aqueous solution after back-extraction has a high rare-earth concentration and contains very few contaminants. A disadvantage of neutral extractants is that the separation factors between pairs of neighbouring rare-earth ions are often small. Another disadvantage of neutral extractants is that they only extract rare earths efficiently from aqueous nitrate or thiocyanate solutions, not from chloride solutions. The performance of basic extractants is somewhat similar to that of neutral extractants, in the sense that they have been used to extract rare earths from nitrate and thiocyanate media (not from a pure chloride medium), and that the rare earths can easily be stripped from the loaded organic phase by neutral or slightly acidified water. For the extraction of rare earths with tetraalkylammonium salts from a nitrate medium, a negative sequence is observed for extraction, i.e. the distribution ratios decrease from lanthanum to lutetium. For extraction of rare earths with tetraalkylammonium salts from a thiocyanate medium, the distribution ratios increase across the lanthanide series (positive extraction sequence). Of interest is the different behaviour of yttrium upon extraction from nitrate or thiocyanate medium: yttrium is situated between neodymium and samarium for extraction with tetraalkylammonium thiocyanates, and between thulium and ytterbium for extraction with tetraalkylammonium nitrates. Based on this *itinerant behaviour* of yttrium, yttrium can rather easily be separated from the other rare

earths by an appropriate choice of the solvent extraction system (US Patent 3,821,352). Combination of neutral and basic extractants in one extracting phase often shows synergistic behaviour, i.e. the distribution ratios for the mixture of extractants is higher than the distribution ratios of the individual extractants. The possibility to extract rare earths from chloride solutions by neutral or basic extractants is highly interesting, because hydrochloric acid is much cheaper and more readily available than nitric acid. It is easier to recycle hydrochloric acid and to use it in a closed-loop process than nitric acid. Waste water treatment of chloride-containing waste streams is easier than treatment of nitrate-containing waste streams. Aqueous thiocyanate solutions suffer from the high price of thiocyanate salts and the limited stability of the thiocyanate ion in strongly acidic aqueous solutions.

Separation of rare earths by solvent extraction is typically carried out from aqueous feed solutions containing chloride or nitrate ions, because rare-earth chloride and nitrate salts have a high solubility in aqueous solutions. The rare-earth sulfates have a much lower solubility in water than the corresponding chlorides or nitrates. However, the possibility to extract rare earths from sulfate medium by neutral or basic extractants is relevant for the rare-earth industry, because leaching of rare-earth ores (bastnäsite, monazite, xenotime, loparite, eudialyte) is often done by sulfuric acid. Rare earths can be present in significant concentrations in the liquors obtained by leaching of uranium ores with sulfuric acid. Extraction of rare earths from sulfate leaching solutions is a method for preconcentration of the rare earths, before the mixture of rare earths is separated into the individual elements. Rare earths can be extracted from sulfate feed solutions by primary amines (basic extractants) or by strongly acidic extractants.

## **SUMMARY OF THE INVENTION**

This invention describes a method to extract rare-earth ions from a concentrated chloride, sulfate or mixed chloride/sulfate aqueous phase to an organic phase, comprising a water-immiscible nitrate or thiocyanate ionic liquid or a mixture of a water-immiscible nitrate or thiocyanate ionic liquid and a neutral extractant. The process allows for the separation of mixtures of rare earths into the different elements, to separate yttrium from the other rare earths, and to separate the rare earths from other metallic elements and/or impurities. The solvent extraction process comprises the following steps: (1) contacting the aqueous feed solution with an organic phase comprising an ionic liquid with nitrate or thiocyanate anions; (2) separating the aqueous phase and the organic phase; (3) scrubbing the organic phase with an aqueous solution of chloride or sulfate salts or water to remove unwanted extracted metal ions from the organic phase; (4)

contacting the resulting loaded organic phase with a stripping solution to selectively strip the rare-earth chlorides or sulfates from the organic phase. The separation of a mixture of two or more metal ions is based on the different extraction efficiencies for the different metal ions. The extraction procedure can be applied by contacting the aqueous phase sequentially with different organic phases. For instance, the aqueous phase can first be contacted with an organic phase containing thiocyanate ions, followed by contacting of the same aqueous phase by an organic phase containing nitrate ions. The concentration of the chloride or sulfate ions in the aqueous phase can be changed before each contact with an organic phase, in order to modify the extraction behavior. In addition to the nitrate or thiocyanate ionic liquid, the organic phase can contain a neutral extractant. Thus in certain embodiments of this invention, the organic phase comprises an ionic liquid with nitrate or thiocyanate anions, in other embodiments said organic phase additionally comprises a neutral extractant; in yet other embodiments said organic phase consists of an ionic liquid with nitrate or thiocyanate anions and a neutral extractant. In addition to the chloride salts, the aqueous feed solution and/or the stripping solution of step (4) can contain a water-soluble organic complexing agent ("complexant"). Thus in certain embodiments of this invention, the aqueous feed solution comprises a complexant, in other embodiments, the stripping solution of step (4) comprises a complexant. In yet another embodiment of the present invention the aqueous feed solution comprises a complexant and the stripping solution of step (4) comprises a complexant. An important aspect of the invention is that chloride and/or sulfate anions are used in the aqueous feed solution to change the percentage extraction by modifying the water activity levels and adding a salting-out effect by using very high ionic strength, whereas anions different to chloride are present in the organic extracting phase for complex formation. The term "*split-anion extraction*" is introduced to describe the solvent extraction process, since different anions are present in the aqueous phase and in the organic phase and the distribution of the ionic liquid anions strongly favors the ionic liquid phase.

The present invention relates to a process for separating a mixture of two or more rare-earth elements, comprising the solvent extraction of rare-earth elements from an aqueous phase comprising  $B^-$  anions to a water-immiscible organic phase comprising an ionic liquid with  $A^-$  anions, wherein  $A^-$  combines with rare-earth elements to form more strongly extracted complexes than  $B^-$ , for example  $A^-$  is nitrate, thiocyanate, or mixtures thereof; and wherein  $B^-$  forms a more weakly extracted complex with rare earths, for example  $B^-$  is chloride, sulfate or mixtures thereof. In addition,  $B^-$  has a lower affinity for the ionic liquid cations than  $A^-$ .

The invention also relates to the extraction of one or more rare-earth elements<sup>5</sup> from an aqueous phase comprising one or more rare-earth elements, and optionally other metallic elements, and B<sup>-</sup> anions to a water-immiscible organic phase comprising an ionic liquid with A<sup>-</sup> anions, wherein A<sup>-</sup> combines with rare-earth elements to form more strongly extracted complexes than B<sup>-</sup>, for example A<sup>-</sup> is nitrate, thiocyanate, or mixtures thereof; and wherein B<sup>-</sup> forms a more weakly extracted complex with rare earths, for example B<sup>-</sup> is chloride, sulfate or mixtures thereof. In addition, B<sup>-</sup> has a lower affinity for the ionic liquid cations than A<sup>-</sup>. In other embodiments of this invention, in particular related to the extraction process of one or more rare-earth elements from an aqueous phase comprising one or more rare-earth elements, and B<sup>-</sup> anions to a water-immiscible organic phase comprising an ionic liquid with A<sup>-</sup> anions, wherein A<sup>-</sup> combines with rare-earth elements to form more strongly extracted complexes than B<sup>-</sup>, wherein A<sup>-</sup> is thiocyanate; and wherein B<sup>-</sup> forms a more weakly extracted complex with rare earths, for example B<sup>-</sup> is chloride, sulfate, nitrate or mixtures thereof. In a more particular embodiment thereof, said B<sup>-</sup> is nitrate.

The concentration of nitrate or thiocyanate ions in the organic phase needs to be high. Therefore, hydrophobic ionic liquids with nitrate or thiocyanate ions are selected as main components of the organic phase. Ionic liquids are solvents that consist entirely of ions. The preferred ionic liquids are the nitrate or thiocyanate salts of the tricaprylmethylammonium (Aliquat 336) or trihexyl(tetradecyl)phosphonium cation, but the invention is not restricted to these specific examples of ionic liquids. The ionic liquids have the general formulae [Q<sup>+</sup>][A<sup>-</sup>], where Q<sup>+</sup> is a cation and A<sup>-</sup> is an anion. Q<sup>+</sup> has the general formula (R<sub>1</sub>)(R<sub>2</sub>)(R<sub>3</sub>)(R<sub>4</sub>)X<sup>+</sup>, wherein X is N, P, As or Sb, but preferably X is N or P. R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub> can be identical or different, and are a linear or branched alkyl chain, a cycloalkyl group or an aromatic group, wherein said alkyl chain, cycloalkyl or aromatic groups are optionally substituted with one or more substituents selected from the group consisting of halogen, hydroxyl, sulfhydryl, amino, cyano, carboxyl, amide, ester and nitro; and wherein said R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, and/or R<sub>4</sub> optionally comprise at least 1 heteroatom, each of said heteroatoms being independently selected from the group consisting of nitrogen, oxygen, sulfur, selenium and phosphorus. The total number of carbon atoms for R<sub>1</sub> + R<sub>2</sub> + R<sub>3</sub> + R<sub>4</sub> is at least 24, preferably between 25 and 40. In an embodiment of the present invention, R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> can be a hydrogen atom, provided that the total number of carbon atoms for R<sub>1</sub> + R<sub>2</sub> + R<sub>3</sub> + R<sub>4</sub> is at least 24. A<sup>-</sup> is an anion capable of complexing rare-earth ions, preferably A<sup>-</sup> is NO<sub>3</sub><sup>-</sup> or SCN<sup>-</sup>. The ionic liquids [Q<sup>+</sup>][A<sup>-</sup>] can be used as a pure compound or as mixtures of two or more [Q<sup>+</sup>][A<sup>-</sup>] compounds. The ionic liquid can be used in a pure undiluted form or it can be mixed with a neutral extractant.

Neutral extractants or solvating extractants are neutral molecules. The neutral extractants have the general formulae  $(R_5)(R_6)(R_7)X=O$ ,  $(R_5O)(R_6O)(R_7O)X=O$ ,  $(R_5)(R_6)(R_7O)X=O$ ,  $(R_5)(R_6O)(R_7)X=O$ ,  $(R_5)(R_6)Z=O$ ,  $(R_5O)(R_6O)Z=O$ .  $R_5$ ,  $R_6$ ,  $R_7$  can be identical or different, and are a hydrogen atom, a linear or branched alkyl chain, a cycloalkyl group or an aromatic group, wherein said alkyl chain, cycloalkyl or aromatic groups are optionally substituted with one or more substituents selected from the group consisting of halogen, hydroxyl, sulfhydryl, amino, cyano, carboxyl, amide, ester and nitro ; and wherein said  $R_1$ ,  $R_2$ ,  $R_3$ , and/or  $R_4$  optionally comprise at least 1 heteroatom, each of said heteroatoms being independently selected from the group consisting of nitrogen, oxygen, sulfur, selenium and phosphorus. The total number of carbon atoms for  $R_5 + R_6 + R_7$  is at least 12, preferably between 12 and 36 (due to viscosity).  $X$  is P, As or Sb, but preferably  $X$  is P.  $Z$  is S, Se, or Te, but preferably  $Z$  is S. The  $X=O$  and  $Z=O$  groups from the neutral extractants can be part of a ring structure, together with  $(R_5)$  and/or  $(R_6)$  and/or  $(R_7)$ . The  $(R_5)(R_6)(R_7)X=O$ ,  $(R_5O)(R_6O)(R_7O)X=O$ ,  $(R_5)(R_6)(R_7O)X=O$ ,  $(R_5)(R_6O)(R_7)X=O$ ,  $(R_5)(R_6)Z=O$ ,  $(R_5O)(R_6O)Z=O$  compounds can be used as pure compounds or as mixtures of two or more of these compounds. Examples of neutral extractants are Cyanex 923, Cyanex 925 or tri-*n*-butylphosphate (TBP), but the invention is not restricted to these specific examples of neutral extractants. Other classes of neutral extractants can be used as well. Examples include crown ethers, glymes, ethers, alcohols, ketones (e.g. methyl isobutyl ketone, MIBK), esters, amides and heterocycles such as 2,2'-bipyridine or 1,10-phenanthroline.

In other embodiments of the present invention, said neutral extractant is an acidic extractant. In very acidic conditions, also acidic extractants can behave as neutral extractants. Examples of acidic extractants include, but are not limited to, the phosphorus-containing extractants bis(2-ethylhexyl)phosphoric acid (HDEHP, D2EHPA or P204), (2-ethylhexyl)phosphonic acid, mono(2-ethylhexyl) ester (HEHEHP, or P507) and bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex 272), the carboxylic acids such as neodecanoic acid (Versatic Acid 10) and naphthenic acids, as well as  $\beta$ -diketones and derivatives of 8-hydroxyquinoline.

In addition to the ionic liquid and the neutral extractant, a fraction of the organic phase can be a diluent, or a diluent and a (phase) modifiers can be added to change physicochemical properties such as solubility, viscosity, interfacial parameters, reducing adsorption losses and preventing third-phase formation. A diluent can be added to change the solubility and/or viscosity. A modifier or phase modifier can be added to change interfacial parameters, to reduce absorption losses and/or to prevent third-phase formation. Said diluents can be aliphatic hydrocarbons, aromatic hydrocarbons, halogenated aliphatic hydrocarbons, halogenated aromatic hydrocarbons, ethers, alcohols



or ketones. The preferred diluents are aromatic hydrocarbons. Examples of such aromatic hydrocarbons include benzene, toluene, ethylbenzene, xylene, or commercial mixtures of aromatic solvents such as the Solvesso aromatic fluids (ExxonMobil Chemical). Typically, the aqueous feed solution contains dissolved rare-earth chlorides, sulfates or mixtures thereof, in concentrations between 1 g/L and 500 g/L, but preferably between 100 g/L and 400 g/L. Extra chloride ions in the aqueous feed solution can be provided by the rare-earth chloride salts, ammonium chloride, alkali metal chlorides, earth-alkaline chlorides, soluble transition metal chlorides or hydrochloric acid. The preferred chloride salts are calcium chloride, magnesium chloride or ammonium chloride. Extra sulfate ions in the aqueous feed solution can be provided by, for example, ammonium sulfate, alkali metal sulfates, magnesium sulfate or sulfuric acid. The preferred sulfate sources are ammonium sulfate and sulfuric acid. The aqueous feed solutions can contain also mixtures of chloride and sulfate ions. The preferred pH is between 1.5 and 6.0., but solutions with a higher acidity can be used. To increase the separation factors for nitrate-based ionic liquids, complexing agents can be added to the aqueous phase. Typical examples are ethylenediaminetetraacetic acid (EDTA), *N*-(hydroxyethyl)-ethylenediaminetriacetic acid (HEDTA), 1,2-diaminocyclohexanetetraacetic acid (DCTA), diethylene triamine pentaacetic acid (DTPA),  $\alpha$ -hydroxyisobutyric acid (HIBA), citric acid, malonic acid or lactic acid.

A certain aspect of the present invention relates to the possibility of changing the distribution ratios by changing the concentration of the chloride or sulfate salts in the aqueous phase. By increasing the concentration of chloride or sulfate salts, the distribution ratios are raised. By starting from a low concentration of chlorides or sulfate salts, the distribution ratios are lowered. Due to significant separation factors this means that, at optimized concentrations (demanded especially for different compositions), groups or individual rare earths can be selectively extracted. The aqueous solution starts at a lower salt concentration and is sequentially contacted with different organic phases; for instance, one contact with a thiocyanate ionic liquid and one with a nitrate ionic liquid. Between the different contacts, the chloride or sulfate concentration in the aqueous solution can be gradually increased by dissolution of extra chloride or sulfate salts.

Another aspect of the present invention relates to contacting the chloride or sulfate aqueous phase sequentially with organic phases containing different anions, for instance contacting the aqueous feed phase with a thiocyanate ionic liquid, followed by contacting the aqueous feed phase with a nitrate ionic liquid. The order of contacting the aqueous feed phase with different ionic liquid can be reversed; first a contact with a nitrate ionic liquid, followed by a thiocyanate ionic liquid.

Yet another aspect of the present invention relates to the selective stripping of the rare-earth chlorides from the loaded organic phase by aqueous stripping solutions containing different concentrations of chloride or sulfate salts. In the case of a nitrate-containing organic phase (nitrate ionic liquid), the aqueous stripping solution can alternatively be a nitrate solution that additionally may comprise one or more complexing agents. In the case of a thiocyanate-containing organic phase (thiocyanate ionic liquid), the aqueous stripping solution can alternatively be a thiocyanate solution that additionally may comprise one or more complexants.

The application of split-anion extraction is not restricted to the use of conventional liquid-liquid extraction (solvent extraction processes), but it can be used in extraction chromatography as well. In extraction chromatography, the organic phase or ionic liquid phase is immobilized on a high-surface area solid support by impregnation (supported ionic liquid phases or SILPs).

Numbered statements of the invention are:

1. A process for removing with an extraction method one or more rare-earth elements from a hydrophilic composition, the process comprising the steps of
  - providing a hydrophilic composition comprising one or more rare-earth elements and one or more rare earth complexing  $B^-$  anions
  - separating one or more rare-earth element from said solution by extraction with a water-immiscible organic phase comprising an ionic liquid with one or more rare earth element complexing  $A^-$  anions,  
wherein the  $A^-$  anion in the water-immiscible organic phase is an anion with a lower hydrophobicity than the  $B^-$  anion in the hydrophilic composition.
2. The process according to statement 1, wherein the one or more  $B^-$  anions are selected from the group consisting of chloride, sulfate and nitrate.
3. The process according to statement 1 or 2, wherein the one or more  $A^-$  anions are nitrate or thiocyanate.
4. The process according to any one of statements 1 to 3, wherein the  $B^-$  anion is chloride and the  $A^-$  anion is nitrate.
5. The process according any one of statements 1 to 4, wherein the hydrophilic composition is an aqueous solution.

6. The process according to anyone of statements 1 to 4, wherein the hydrophilic composition is a molten salt phase, a molten salt hydrate phase or an ionic liquid phase, wherein these phases are immiscible with the organic phase.
7. The process according to any one of statements 1 to 6, wherein the organic phase is immobilized or impregnated on a solid support.
8. The process according to any one of statements 1 to 7, wherein the organic phase comprises an ionic liquid selected from the group consisting of tricaprylmethylammonium nitrate, tricaprylmethylammonium thiocyanate, trihexyl(tetradecyl)phosphonium nitrate and trihexyl(tetradecyl)phosphonium thiocyanate.
9. The process according to any one of statements 1 to 8, wherein a neutral extractant has been dissolved in the organic phase.
10. The process according to statement 9, wherein the neutral extractant is tri-*n*-butylphosphate (TBP), or is a mixture of tri(*n*-hexyl)phosphine oxide and tri(*n*-octyl)phosphine oxide (Cyanex 923), or is a mixture of bis(2,4,4-trimethylpentyl) *n*-octylphosphine oxide and tris(2,4,4-trimethylpentyl)phosphine oxide (Cyanex 925).
11. The process according to any one of statements 1 to 10, wherein the organic phase further comprises a diluent.
12. The process according to any one of statements 1 to 11, wherein a water-soluble complexing agent is added to the hydrophilic composition.
13. The process according to any one of statements 1 to 12, wherein the hydrophilic composition is repeatedly extracted with organic phase.
14. The process according to statement 13, wherein the hydrophilic composition is sequentially, and at least twice, extracted with organic phases of a different composition.
15. The process according to statement 13 or 14, wherein the concentration of anion B<sup>-</sup> in the hydrophilic composition is varied in the individual extractions, for example by dissolution of salts containing anion B<sup>-</sup> or by dilution.

16. The process according to 15, wherein the concentration of anion  $B^-$  is increased by addition of a compound selected from the group consisting of calcium chloride, magnesium chloride, nickel(II) chloride, lithium chloride, ammonium chloride, a mixture of lithium- and ammonium-chloride, and ammonium sulfate.
17. The process according to statement 13 or 14, which is a continuous process wherein the concentration of anion  $B^-$  in the hydrophilic composition is continuously increased or decreased, for example by respectively the dissolution of salts containing anion  $B^-$  or dilution with water.
18. The process according to any of statements 13 to 15, which is at least a two-step process, wherein the hydrophilic composition is sequentially contacted with the organic phase, wherein at least in one step a different concentration of anion  $B^-$  is used in the hydrophilic composition.
19. The process according to any one of statements 1 to 11, wherein yttrium is separated from the other rare-earth elements, which is at least a two-step process, wherein the hydrophilic composition comprising chloride anions as  $B^-$  anions is contacted with an organic phase comprising an ionic liquid and nitrate anions as  $B^-$  anions, followed by a second contact of the hydrophilic composition with an organic phase comprising an ionic liquid and thiocyanate anions as  $B^-$  anions, whereby the yttrium remains in the hydrophilic composition and the other rare-earth elements are extracted to the organic phases.
20. The process according to statement 18, wherein the aqueous phase is first extracted with an organic phase wherein  $A^-$  is nitrate, followed by a second extraction with an organic phase wherein  $A^-$  is thiocyanate.
21. The process according to statement 18, wherein the aqueous phase is first extracted with an organic phase wherein  $A^-$  is thiocyanate, followed by a second extraction with an organic phase wherein  $A^-$  is nitrate.
22. The process according to any one of statements 1 to 21, further comprising the step of selectively or complete isolating rare-earth elements from the organic phase by stripping with water or with an aqueous phase comprising a rare earth complexing anion  $B^-$  in a concentration that is lower compared to the  $B^-$  anion concentration in the hydrophilic composition before extraction.

23. The process according to statement 22, wherein the  $B^-$  anion in the stripping solution is the same anion as the  $B^-$  anion in the hydrophilic composition before extraction, for example said  $B^-$  anion is chloride.
24. Use of an ionic liquid with rare-earth element complexing anions to remove one or more rare earth elements from a hydrophilic composition, by contacting said hydrophilic composition, comprising one or more rare-earth elements and one or more rare earth complexing  $B^-$  anions, with a water-immiscible organic phase, comprising said ionic liquid with one or more rare earth element complexing  $A^-$  anions, wherein the  $A^-$  anion in the water-immiscible organic phase is an anion with a lower hydrophobicity than the  $B^-$  anion in the hydrophilic composition.

Further numbered statements of the invention are as follows:

1. A process for separating a mixture of two or more rare-earth elements, comprising the solvent extraction of rare-earth elements from an aqueous phase comprising  $B^-$  anions to a water-immiscible organic phase comprising an ionic liquid with  $A^-$  anions, wherein  $A^-$  is nitrate, thiocyanate, or mixtures thereof; and wherein  $B^-$  is chloride, sulfate or mixtures thereof.
2. The process according to statement 1, wherein a neutral extractant has been dissolved in the organic phase.
3. The process according to statement 1 or 2, wherein the organic phase further comprises an organic molecular diluent.
4. The process according to any one of statements 1 to 3, wherein a water-soluble complexing agent is added to the aqueous phase.
5. The process according to any one of statements 1 to 4, wherein the aqueous phase is sequentially contacted with different batches of the organic phases and wherein between the different contacts the concentration of anion  $B^-$  in the aqueous solution optionally varied, for example by dissolution of salts containing anion  $B^-$  or by dilution.
6. The process according to statement 5, wherein the sequential contact is a continuous process wherein the concentration of anion  $B^-$  in the aqueous solution is continuously increased or decreased, for example by dissolution of salts containing anion  $B^-$  or dilution with water.
7. The process according to statement 5, wherein the sequential contact is at least a two-step process, wherein the aqueous phase is sequentially contacted with different batches of the organic phases in each step, wherein at least in one step a different concentration of anion  $B^-$  is used in the aqueous solution.

8. The process according to any one of statements 1 to 7, wherein the aqueous phase is sequentially, and at least twice, contacted with organic phases of different compositions.
9. The process according to any one of statements 1 to 7, wherein the organic phase after contacting with the aqueous phase is contacted with one or more aqueous phases comprising varying concentrations of anion B<sup>-</sup> to selectively or totally remove extracted rare-earth elements from the organic phase.
10. The process according to any one of statements 1 to 7, wherein the organic phase after contacting with the aqueous phase is contacted with one or more aqueous phases comprising varying concentrations of anion A<sup>-</sup> to selectively or totally remove extracted rare-earth elements from the organic phase.
11. The process according to anyone of statements 1 to 3, wherein the aqueous phase is replaced by a molten salt phase, a molten salt hydrate phase or an ionic liquid phase, wherein these phases are immiscible with the organic phase.
12. The process according to any one of statements 1 to 11, wherein yttrium is separated from the other rare earth elements.
13. The process according to any one of statements 1 to 12, wherein the organic phase comprises the ionic liquid tricaprylmethylammonium nitrate.
14. A process according to any one of statements 1 to 12, wherein the organic phase comprises an ionic liquid, which is tricaprylmethylammonium thiocyanate.
15. A process according to any one of statements 1 to 12, wherein the organic phase comprises an ionic liquid, which is trihexyl(tetradecyl)phosphonium nitrate.
16. A process according to any one of statements 1 to 12, wherein the organic phase comprises an ionic liquid, which is trihexyl(tetradecyl)phosphonium thiocyanate.
17. The process according to any one of statements 2 to 16, wherein the neutral extractant is tri-*n*-butylphosphate (TBP).
18. The process according to any one of statements 2 to 16, wherein the neutral extractant is a mixture of tri(*n*-hexyl)phosphine oxide and tri(*n*-octyl)phosphine oxide (Cyanex 923)
19. The process according to any one of statements 2 to 16, wherein the neutral extractant is a mixture of bis(2,4,4-trimethylpentyl) *n*-octylphosphine oxide and tris(2,4,4-trimethylpentyl)phosphine oxide (Cyanex 925).
20. The process according to any of statements 1, 2, 3 and 5, wherein the aqueous phase is first contacted with an organic phase wherein A<sup>-</sup> is nitrate, followed by a second contact with an organic phase wherein A<sup>-</sup> is thiocyanate.
21. The process according to any of statements 1, 2, 3, 4 and 8, wherein the aqueous phase is first contacted with an organic phase wherein A<sup>-</sup> is thiocyanate, followed by a second contact with an organic phase wherein A<sup>-</sup> is nitrate.

22. The process according to any of statements 5, 6, 7 and 9, wherein concentration of anion B<sup>-</sup> in the aqueous phase is varied by addition of calcium chloride.
23. The process according to any of statements 5, 6, 7 and 9, wherein concentration of anion B<sup>-</sup> in the aqueous phase is varied by addition of magnesium chloride.
24. The process according to any of statements 5, 6, 7 and 9, wherein concentration of anion B<sup>-</sup> in the aqueous phase is varied by addition of nickel(II) chloride.
25. The process according to any of statements 5, 6, 7 and 9, wherein concentration of anion B<sup>-</sup> in the aqueous phase is varied by addition of ammonium sulfate.
26. The process according to any of claims 5, 6, 7 and 9, wherein concentration of anion B<sup>-</sup> in the aqueous phase is varied by addition of ammonium chloride and/or lithium chloride.
27. The use of quaternary phosphonium salts with thiocyanate anions for solvent extraction processes.
28. The use of trihexyl(tetradecyl)phosphonium thiocyanate for solvent extraction processes.
29. The process according to any of claims 1 to 26, wherein the B<sup>-</sup> anions additionally comprise thiocyanate anions, e.g. by adding a thiocyanate salt.
30. The process according to any of claims 1 to 26, wherein the B<sup>-</sup> anions additionally comprise nitrate anions, e.g. by adding a nitrate salt.
31. The process according to any of claims 1 to 26, wherein the A<sup>-</sup> anions additionally comprise perchlorate or chloride anions.
32. The process according to any of claims 1 to 26, wherein the A<sup>-</sup> anions additionally comprise perchlorate or chloride anions and B<sup>-</sup> anions additionally comprise thiocyanate anions, e.g. by adding a thiocyanate salt.
33. The process according to any of claims 1 to 26, wherein the A<sup>-</sup> anions additionally comprise perchlorate or chloride anions and B<sup>-</sup> anions additionally comprise nitrate anions, e.g. by adding a nitrate salt.

## DETAILED DESCRIPTION OF THE INVENTION

### Definitions:

"Rare earths" or "rare-earth elements" (REEs) in the context of the present invention relates to the whole group of 17 *rare earths* or *rare-earth elements* (REEs): scandium (Sc), yttrium (Y), lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb) and lutetium (Lu). Subgroups are the light rare-earth elements (LREEs): lanthanum (La),

cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu) and gadolinium (Gd); and the heavy rare-earth elements (HREEs): terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb) and lutetium (Lu). REE stands for rare-earth element.

$B^-$  anions and  $A^-$  anions refers to REE complexing anions of organic liquids. Anions are classified as  $B^-$  or  $A^-$  depending on their preference for residing in an aqueous hydrophilic phase is in a hydrophilic/hydrophobic two-component system. The order of hydrophylicity is  $SO_4^{2-} > Cl^- > Br^- > NO_3^- > I^- > ClO_4^- > SCN^-$ . This order corresponds to the Hofmeister series or lyotropic series. Thus, for example,  $NO_3^-$  and  $SCN^-$  anions have a lower hydrophylicity as compared to  $SO_4^{2-}$  and  $Cl^-$ . In the context of the present invention anions in the hydrophilic composition are  $B^-$  and anions in the organic phase are  $A^-$  if the anion in the organic phase has a higher lyotropic effect than the anion in the hydrophilic phase. The classification thus depends on a comparison between anions.

Examples of possible combinations are:

$B^-$ anions	$A^-$ anions
$Cl^-$	$NO_3^-$
$Cl^-$	$SCN^-$
$SO_4^{2-}$	$NO_3^-$
$SO_4^{2-}$	$SCN^-$
$NO_3^-$	$SCN^-$

As a consequence of the fact that relative properties are considered, nitrate can be an  $A^-$  or  $B^-$  anion depending on the other anion that is used.

In an embodiment of the present invention, the  $B^-$  anions are selected from the group consisting of chloride, sulfate and nitrate and the  $A^-$  anions are selected from the group consisting of nitrate or thiocyanate. In a specific embodiment of the present invention, the  $B^-$  anions are selected from the group consisting of chloride, sulfate and nitrate and the  $A^-$  anions are selected from the group consisting of nitrate or thiocyanate, provided that  $B^-$  anions and  $A^-$  anions are not both nitrate.

In another specific embodiment of the present invention, the  $B^-$  anions are selected from the group consisting of chloride, sulfate and nitrate or any mixtures of chloride and/or sulfate and/or nitrate.



In another specific embodiment of the present invention, the A<sup>-</sup> anions are selected from the group consisting of nitrate or thiocyanate or any mixture of nitrate and thiocyanate.

*"Solvent extraction"* refers to the distribution of a solute between two immiscible liquid phases in contact with each other, i.e. a two-phase distribution of a solute. In this invention, the solute is a rare-earth element, which can be in the form of a rare-earth salt. A rare-earth salt is a rare-earth ion and one or more anions. Of particular interest in this invention are chloride, nitrate and sulfate salts. Solvent extraction, as applied to hydrometallurgy, is a unit operation for the purification and concentration of a wide variety of metals. In this invention, the metals of interest are rare-earth elements. In general, solvent extraction comprises a step wherein an aqueous phase containing the metal of interest is contacted with an organic phase comprising an extractant.. In the context of the present invention, said aqueous phase can be any hydrophilic composition which is immiscible with the organic phase. The extractant chemically reacts with the metal to form an organic-metal complex that is soluble in the organic phase. Impurities normally do not react with the extractant and remain in the aqueous phase. The organic phase, containing the organic-metal complex, is separated from the aqueous phase. The metal is recovered and concentrated into another aqueous phase by reversing the chemical reaction. Solvent extraction is often abbreviated to SX. "Liquid-liquid extraction" or "liquid-liquid distribution" are sometimes used as synonyms for solvent extraction.

"Extraction" is the operation of transferring the metal of interest from the aqueous phase or hydrophilic composition phase ("SX feed", "aqueous feed" or "aqueous feed solution") to the organic phase. The extraction circuit produces a loaded organic phase containing the metal value and an aqueous phase depleted of the metal known as raffinate. The raffinate is sent for further treatment or effluent.

*"Scrubbing"* (or *"washing"*) is the selective removal of impurity metals from the loaded organic phase by treatment with either fresh scrub solution or a bleed of the strip liquor. The spent scrub solution is normally combined with the aqueous feed solution. The scrubbed organic phase containing the metal of interest is advanced to stripping.

*"Stripping"* (or *"back extraction"*) is the process of removing the metal of value from the scrubbed organic phase by reversing the extraction chemical reaction. In the context of the present invention, the metal of value is a REE. It is normally conducted under conditions in order to produce a strip liquor containing a high concentration of the metal value. The strip liquor is the product of the solvent extraction circuit. General Stripping refers to the (non-selective) stripping of the main solute(s) present, usually in one general stripping step. The term *"selective stripping"* is used where two or more main solutes are stripped successively from an extract, usually with different stripping agents

with a view to their subsequent separate recovery from solution. "*Regeneration*" is the treatment of the stripped organic phase for removal of metals that were not scrubbed or stripped, or for the removal of organic degradation products. The operation produces a regenerated organic phase for recycle to the extraction operation as organic feed. The spent regenerant is advanced for further processing or to effluent treatment.

"Removing" one or more rare-earth elements in the context of the present invention refers to the transfer of at least one REE to an organic phase. Depending from the reaction conditions a rare earth element is after an extraction step for at least 10, 20, 25, 50, 75, 90, 95, 99, 99.5 or 99.9 % present in the organic phase. Depending from the reaction conditions, when starting from a mixture of REEs in the hydrophilic composition or aqueous phase, the organic phase can contain different elements in different concentrations. The methods of the present invention accordingly allow to provide fractions which are enriched for a certain REE. This is typically achieved by batchwise or continuous repeatedly extractions. The methods of the present invention also allow to transfer in a single extraction step as much as possible of as a many as possible REEs to the organic phase. "*Crowding*" is the displacement of an impurity from an extract phase by contact with a solution containing the main extractable solute. The main solute need not be present in a pure solution but should have a higher distribution ratio than the impurities present. The "*extract*" is the separated phase (often but not necessarily organic) that contains the material extracted from the other phase. The "*raffinate*" is the phase remaining after extraction of some specified solute(s).

The "*distribution ratio*" (D) is the ratio of the total analytical concentration of a solute in the extract (regardless of its chemical form) to its total analytical concentration in the other phase. The "*separation factor*" is the ratio of the respective distribution ratios of two extractable solutes measured under the same conditions. The "*loading*" is the concentration of an extracted solute in the extract. The term "loaded solvent" is used to denote the extract after completion of a particular step, e.g. extraction or scrubbing. The "*phase ratio*" is the ratio of the quantity of the solvent to that of the other phase. Unless otherwise specified the phase ratio refers to the "*phase volume ratio*".

The "*extractant*" (or "*extracting agent*") is the active component primarily responsible for transfer of a solute from one phase to the other. Certain extractants that consist of liquids immiscible with water might comprise the only component of the initial organic phase but extractant(s) can also be dissolved in diluents. One distinguishes three distinct classes of extractants: (1) *acidic extractants*, such as the phosphorus-containing extractants bis(2-ethylhexyl)phosphoric acid (HDEHP, D2EHPA or P204), (2-ethylhexyl)phosphonic acid, mono(2-ethylhexyl) ester (HEHEHP, or P507) and bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex 272), as well as carboxylic acids such as

neodecanoic acid (Versatic Acid 10) and naphthenic acids; (2) *basic extractants* or *anion exchangers* such as quaternary ammonium salts (e.g. Aliquat 336); and (3) "*neutral extractants*" or "*solvating extractants*" (both terms have the same meaning throughout this specification), such as tri-*n*-butylphosphate (TBP), Cyanex 923 or Cyanex 925. Cyanex 923 is a mixture of 60% tri(*n*-hexyl)phosphine oxide and 40% tri(*n*-octyl)phosphine oxide. Cyanex 925 is a mixture of 85% bis(2,4,4-trimethylpentyl) *n*-octylphosphine oxide and 15% tris(2,4,4-trimethylpentyl)phosphine oxide. *Other classes of neutral extractants can be used as well. Examples include crown ethers, glymes, ethers, alcohols, ketones (e.g. methyl isobutyl ketone, MIBK), esters, amides and heterocycles such as 2,2'-bipyridine or 1,10-phenanthroline.* A common feature of neutral extractants is that they consist of neutral molecules with one or more donor atoms such as an oxygen atom, a nitrogen atom, a sulfur atom or a phosphorus atom.

A "diluent" is the liquid or homogeneous mixture of liquids in which extractant(s) and possible modifier(s) may be dissolved to form the solvent phase. Said diluent can be a molecular organic solvent (molecular diluent or organic molecular diluent) or an ionic organic solvent (ionic liquid diluent). Said molecular diluents can be aliphatic hydrocarbons, aromatic hydrocarbons, halogenated aliphatic hydrocarbons, halogenated aromatic hydrocarbons, ethers, alcohols or ketones. The preferred molecular diluents are aromatic hydrocarbons. Examples of such aromatic hydrocarbons/diluents include benzene, toluene, ethylbenzene, xylene, or commercial mixtures of aromatic solvents such as the Solvesso aromatic fluids (ExxonMobil Chemical). In this invention, quaternary ammonium or phosphonium salts with perchlorate anions are used as ionic liquid diluent. A "modifier" is a substance that can be added to the organic phase to change physicochemical properties such as solubility, interfacial parameters, reducing adsorption losses and preventing third-phase formation. The term "solvent" applies to the whole initial liquid phase containing the extractant. The solvent may contain only extractant or it may be a composite homogeneous mixture of extractant(s) with diluent(s) and also sometimes modifiers. In this context the term "organic phase" is often used instead of "solvent". A "water-soluble complexing agent" is a molecule that binds to the rare-earth ions in the aqueous phase. In the context of the present invention, it refers to an agent that can dissolve in water, and increases the separation factors when added to the aqueous phase. Typical examples are ethylenediaminetetraacetic acid (EDTA), N-(hydroxyethyl)-ethylenediaminetriacetic acid (HEDTA), 1,2-diaminocyclohexanetetraacetic acid (DCTA), diethylene triamine pentaacetic acid (DTPA),  $\alpha$ -hydroxyisobutyric acid (HIBA), citric acid, malonic acid or lactic acid.

An "ionic liquid" is a solvent that consists entirely of ions (cations and anions). In this invention, ionic liquids are used as solvent for the extraction processes. An ionic liquid

can act as a diluent, an extractant or as both extractant or diluents. An hydrophobic ionic liquid is an ionic liquids that phase-separates from an aqueous solution. It is understood that the different rare earths in the mixtures do not need to be present in equimolar concentrations. The ratios of the rare earths present in the mixtures to be separated can reflect the natural abundance in the different rare-earth ores. For instance, bastnäsite and monazite are rich in LREEs, whereas xenotime and eudialyte are rich in HREEs and yttrium. General trends are that the abundance of the lanthanides decreases with increasing atomic number and that there is an odd-even effect (elements with an odd atomic number are less abundant than elements with an even atomic number). Cerium is often removed from a rare-earth concentrate in a preliminary step, i.e. before step (1) in the extraction process of this invention, thus before the mixture of rare earths is separated in the individual elements. The rare-earth concentrate obtained by recycling of rare earths from permanent magnets, lamp phosphors, nickel metal hydride batteries or polishing powders has an elemental composition that is quite different from that of rare-earth ores. In general, the number of different rare-earth present in these concentrates is much smaller than in the concentrates obtained from rare-earth ores. For instance, neodymium magnets contain neodymium, praseodymium, dysprosium and terbium, but no other rare earths. Lamp phosphors contain mainly yttrium, europium, lanthanum and terbium, with smaller amounts of cerium and gadolinium. Because the HREEs occur together with large amounts of yttrium, an efficient process for separation of yttrium from HREEs is important.

The invention applies to both the extraction of the rare earths as a group from other elements or the separation of a mixture of two or more rare earths into the individual elements. In case of a process with the purpose of extracting the rare earths as a group from other elements, the aqueous feed solution is obtained by leaching rare earths from ores (bastnäsite, monazite, xenotime, loparite, eudialyte) by aqueous solutions of hydrochloric acid, nitric acid or sulfuric acid. The rare-earth solutions can also be obtained by dissolution of rare-earths in reclaimed rare-earth magnets, lamp phosphors, nickel metal hydride batteries or polishing powders. The aqueous feed solution is prepared for extraction by adding extra chloride or sulfate salts to the leachates. The rare earths are extracted from the type of aqueous feed solutions as a group and the extraction process acts as a preconcentration step for making a rare-earth concentrate.

In case of a process for the separation of a mixture of two or more rare earths into the individual elements, the aqueous feed solution is prepared from a rare-earth concentrate. The concentrate can be mixed rare-earth chlorides, rare-earth sulfates, rare-earth oxides, rare-earth hydroxides or rare-earth carbonates. The mixed rare-earth

chlorides or rare-earth sulfates can be directly dissolved in the aqueous feed phase. The rare-earth chlorides or rare-earth sulfates can be anhydrous or hydrated salts. The rare-earth oxides, hydroxides and carbonates can be dissolved in the aqueous feed phase by using a hydrochloric acid or a sulfuric acid solution. Different concentrations of rare-earth chlorides or sulfates can be used, between 1 g/L and 500 g/L, but preferably between 100 g/L and 400 g/L. The concentrations can be different depending on composition. Concentrated solutions of rare-earth chlorides or rare-earth sulfates are preferred, because of the possibility of these salts to act as their own salting-out agent (inner salting-out effect or self salting-out effect). Highly acidic solutions ( $\text{pH} < 0.5$ ) should be avoided to reduce the decomposition of the thiocyanate ion. The extraction process is relatively independent of the pH, but the pH has to be lower than 6.0 to avoid hydrolysis of the dissolved rare-earth ions. The extraction process in step (1) is efficient at high chloride or sulfate concentrations. Part of the chloride ions can be provided by the dissolved rare-earth chlorides, but in general extra chloride salts have to be added to the aqueous feed solution besides the rare-earth chlorides. Possible chloride salts are ammonium chloride, alkali metal chlorides ( $\text{LiCl}$ ,  $\text{NaCl}$ ,  $\text{KCl}$ ,  $\text{RbCl}$ ,  $\text{CsCl}$ ), earth-alkaline chlorides ( $\text{MgCl}_2$ ,  $\text{CaCl}_2$ ,  $\text{SrCl}_2$ ,  $\text{BaCl}_2$ ), soluble transition metal chlorides ( $\text{NiCl}_2$ ,  $\text{CoCl}_2$ ) or hydrochloric acid ( $\text{HCl}$ ). The preferred chloride salts are calcium chloride ( $\text{CaCl}_2$ ), magnesium chloride ( $\text{MgCl}_2$ ) or ammonium chloride ( $\text{NH}_4\text{Cl}$ ). Extra chloride ions can also be provided by a hydrogen chloride ( $\text{HCl}$ ) solution. In the case that the solution is too acidic, the acid can be neutralized by addition of an oxide or hydroxide of an alkali metal or an alkaline earth metal. Preferred compounds for neutralization are  $\text{MgO}$ ,  $\text{Mg}(\text{OH})_2$ ,  $\text{CaO}$  or  $\text{Ca}(\text{OH})_2$ . Extra sulfate ions can be provided by ammonium sulfate ( $(\text{NH}_4)_2\text{SO}_4$ ), magnesium sulfate ( $\text{MgSO}_4$ ), by alkali sulfates ( $\text{Li}_2\text{SO}_4$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{K}_2\text{SO}_4$ ,  $\text{Rb}_2\text{SO}_4$ ,  $\text{Cs}_2\text{SO}_4$ ), or by sulfuric acid ( $\text{H}_2\text{SO}_4$ ). The preferred sulfate source is ammonium sulfate. In case of working with the LREE and sulfates, the conditions for split-anion extraction have to be chosen in such a way that formation of a precipitate of rare-earth alkali metal or rare-earth ammonium sulfate double salts,  $\text{REE}_2(\text{SO}_4)_3 \cdot \text{M}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$  ( $\text{REE}$  = rare earth,  $\text{M}$  =  $\text{Na}$ ,  $\text{K}$ ,  $\text{NH}_4$ ) is avoided. To increase the separation factors for extraction with nitrate ionic liquids, complexing agents (complexants) can be added to the aqueous feed solution. Typical examples of such complexing agents are ethylenediaminetetraacetic acid ( $\text{EDTA}$ ),  $\text{N}$ -(hydroxyethyl)-ethylenediaminetriacetic acid ( $\text{HEDTA}$ ), 1,2-diaminocyclohexanetetraacetic acid ( $\text{DCTA}$ ), diethylene triamine pentaacetic acid ( $\text{DTPA}$ ),  $\alpha$ -hydroxyisobutyric acid ( $\text{HIBA}$ ), citric acid, malonic acid or lactic acid.  $\text{EDTA}$  is the preferred complexing agent, since the other complexing agents often lead to formation of precipitates.

Although the feed phase of a solvent extraction process is typically an aqueous feed solution, non-aqueous feed solutions are feasible in step (1) as well. Examples

include low-melting anhydrous inorganic salts, molten salt hydrates or ionic liquids that are mutually immiscible with the ionic liquids in the extracting phase. Preferably, the non-aqueous feed phases have chloride or sulfate ions.

The concentration of nitrate or thiocyanate ions in the organic phase needs to be high. Therefore, hydrophobic ionic liquids with nitrate or thiocyanate ions are selected as main components of the organic phase. Ionic liquids are solvents that consist entirely of ions. The ionic liquids have the general formulae  $[Q^+][A^-]$ , where  $Q^+$  is a cation and  $A^-$  is an anion.  $Q^+$  has the general formula  $(R_1)(R_2)(R_3)(R_4)X^+$ , wherein X is N, P, As or Sb, but preferably X is N or P.  $R_1, R_2, R_3, R_4$  can be identical or different, and are a linear or branched alkyl chain, a cycloalkyl group or an aromatic group, wherein said alkyl chain, cycloalkyl or aromatic groups are optionally substituted with one or more substituents selected from the group consisting of halogen, hydroxyl, sulfhydryl, amino, cyano, carboxyl, amide, ester and nitro ; and wherein said  $R_1, R_2, R_3$ , and/or  $R_4$  optionally comprise at least 1 heteroatom, each of said heteroatoms being independently selected from the group consisting of nitrogen, oxygen, sulfur, selenium and phosphorus. The total number of carbon atoms for  $R_1 + R_2 + R_3 + R_4$  is at least 24, preferably between 25 and 40. In an embodiment of the present invention,  $R_1, R_2, R_3$  and  $R_4$  can be a hydrogen atom, provided that the total number of carbon atoms for  $R_1 + R_2 + R_3 + R_4$  is at least 24.  $A^-$  is an anion capable of complexing rare-earth ions, preferably  $A^-$  is  $NO_3^-$  or  $SCN^-$ . The ionic liquids  $[Q^+][A^-]$  can be used as a pure compound or as mixtures of two or more  $[Q^+][A^-]$  compounds. The ionic liquid can be used in a pure undiluted form or it can be mixed with a neutral extractant. The preferred ionic liquids are the nitrate or thiocyanate salts of the tricaprylmethylammonium (Aliquat 336) or trihexyl(tetradecyl)phosphonium cation, but the invention is not restricted to these specific examples of ionic liquids. Other cations of interest are substituted imidazolium, pyridinium, pyrrolidinium, morpholinium, piperidinium, sulfonium and guanidinium. Requirements are that the ionic liquids in combination with a nitrate or thiocyanate anion phase-separates from the aqueous phase and has a very low solubility in water or preferably said ionic liquid is immiscible with water. Neutral extractants are neutral molecules, without acidic hydrogen atoms. Said neutral extractants have the general formulae  $(R_5)(R_6)(R_7)X=O$ ,  $(R_5O)(R_6O)(R_7O)X=O$ ,  $(R_5)(R_6)(R_7O)X=O$ ,  $(R_5)(R_6O)(R_7)X=O$ ,  $(R_5)(R_6)Z=O$ ,  $(R_5O)(R_6O)Z=O$ .  $R_5, R_6, R_7$  can be identical or different, and are a hydrogen atom, a linear or branched alkyl chain, a cycloalkyl group or an aromatic group, wherein said alkyl chain, cycloalkyl or aromatic groups are optionally substituted with one or more substituents selected from the group consisting of halogen, hydroxyl, sulfhydryl, amino, cyano, carboxyl, amide, ester and nitro ; and wherein said  $R_1, R_2, R_3$ , and/or  $R_4$  optionally comprise at least 1 heteroatom, each of said heteroatoms being independently selected from the group consisting of nitrogen, oxygen, sulfur, selenium and phosphorus. The total number of carbon atoms

for  $R_5 + R_6 + R_7$  is at least 12, but less than 36. In said neutral extractants, X is P, As, Sb, but preferably X is P and Z is S, Se or Te, but preferably Z is S. The X=O and Z=O groups can be part of a ring structure, together with ( $R_5$ ) and/or ( $R_6$ ) and/or ( $R_7$ ). The ( $R_5$ )( $R_6$ )( $R_7$ )X=O, ( $R_5O$ )( $R_6O$ )( $R_7O$ )X=O, ( $R_5$ )( $R_6$ )( $R_7O$ )X=O, ( $R_5$ )( $R_6O$ )( $R_7$ )X=O, ( $R_5$ )( $R_6$ )Z=O, ( $R_5O$ )( $R_6O$ )Z=O compounds can be used as pure compounds or as mixtures of two or more of these compounds. Examples of such neutral extractants are Cyanex 923, Cyanex 925 or tri-*n*-butylphosphate (TBP), but the invention is not restricted to these specific examples of neutral extractants. Other classes of neutral extractants can be used as well. Examples include crown ethers, glymes, ethers, alcohols, ketones (e.g. methyl isobutyl ketone, MIBK), esters, amides and heterocycles such as 2,2'-bipyridine or 1,10-phenanthroline. In very acidic conditions (more specifically  $\text{pH} < 1$ ), also acidic extractants can behave as neutral extractants. Examples of acidic extractants include the phosphorus-containing extractants bis(2-ethylhexyl)phosphoric acid (HDEHP, D2EHPA or P204), (2-ethylhexyl)phosphonic acid, mono(2-ethylhexyl) ester (HEHEHP, or P507) and bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex 272). Other examples include carboxylic acids such as neodecanoic acid (Versatic Acid 10) and naphthenic acids, as well as  $\beta$ -diketones and derivatives of 8-hydroxyquinoline. In another embodiment of the invention a fraction of the organic phase can be a diluent, such as a molecular organic diluent in addition to the ionic liquid and the neutral extractant. Said diluents can be aliphatic hydrocarbons, aromatic hydrocarbons, halogenated aliphatic hydrocarbons, halogenated aromatic hydrocarbons, ethers, alcohols or ketones. The preferred diluents are aromatic hydrocarbons such as benzene, toluene, ethylbenzene, xylene, or commercial mixtures of aromatic solvents such as the Solvesso aromatic fluids (ExxonMobil Chemical). The dry ionic liquids  $[Q^+][A^-]$  often have a high viscosity. The viscosity can be lowered by using diluents, such as organic molecular diluents, or by performing the extractions at elevated temperatures, between room temperature and 100 °C. However, presaturation of the ionic liquid phase by an aqueous solution is often sufficient to lower the viscosities to acceptable values. The combination of ionic liquids with neutral extractants also leads to organic phases with lower viscosities. Phase modifiers can be added to the organic phase to change physicochemical properties such as solubility, interfacial parameters, reducing adsorption losses and preventing third-phase formation. Typically phase modifiers are long-chain alcohols such as 1-decanol, isodecanol, 2-ethylhexanol and nonylphenol.

The ratio of the volumes of the the organic phase and the aqueous feed solution (phase ratio) can be varied. The volume of the organic phase should be sufficiently high in order to avoid exceeding the loading capacity of the organic phase. In cases where the organic phase consists only of an ionic liquid (and not added neutral extractant), the loading of the organic phase is preferably kept below 40 g/L. However, higher loadings

can be achieved by adding a neutral extractant to the ionic liquid organic phase. A diluent such as an organic molecular diluent in the organic phase should be used only if the viscosity of the organic phase is too high for convenient processing. The distribution ratios can be raised by addition of thiocyanate salts such as KSCN, NaSCN or NH<sub>4</sub>SCN to the aqueous phase, but this increases the amount of thiocyanate ions present in the aqueous phase. The same effect can be obtained by addition of nitrate salts such as KNO<sub>3</sub>, NaNO<sub>3</sub> or NH<sub>4</sub>NO<sub>3</sub> to the aqueous phase.

The fact that ionic liquids with nitrate or thiocyanate ions can be used in combination with aqueous feed phases containing chloride (or sulfate) ions is based on the observation that chloride ions (or sulfate ions) have a stronger tendency to reside in the aqueous phase than in the organic phase as counter anion of an ionic liquid cation. The order of preference for residing in the aqueous phase is: SO<sub>4</sub><sup>2-</sup> > Cl<sup>-</sup> > Br<sup>-</sup> > NO<sub>3</sub><sup>-</sup> > I<sup>-</sup> > ClO<sub>4</sub><sup>-</sup> > SCN<sup>-</sup>. This order corresponds to the Hofmeister series or lyotropic series. Depending on the cation, there might be reversal of the order at some places, but chloride or sulfate ions always have a stronger tendency to remain in the aqueous phase than nitrate or thiocyanate. The order also reflects the hydration numbers of the different anions. For this reason, hydrophobic quaternary ammonium chlorides such as tricaprylmethylammonium chloride (Aliquat 336) can be transformed in their nitrate form by contacting the chloride salt with a concentrated aqueous solution of a water-soluble nitrate salt. In the same way, hydrophobic quaternary ammonium chlorides can be transformed into the thiocyanate form by contacting the chloride salt with a concentrated aqueous solution of a water-soluble thiocyanate salt.

Typically, the extraction process according to this invention makes use of aqueous feed solutions containing high concentrations of chloride ions, sulfate ions or mixtures of chloride and sulfate ions. However, it is also possible to apply the split-anion extraction to the extraction of rare earths from aqueous feed solutions with high nitrate concentrations by thiocyanate ionic liquids, because thiocyanate anions have a much higher affinity for the ionic liquid phase than nitrate ions. Based on the concepts presented in this invention, it is possible to design other split-anion extraction systems. The main requirement is that the anion of the ionic liquid in the organic phase has a stronger affinity for the organic phase than for the aqueous phase. This also implies that the anion in the aqueous phase has a stronger tendency for the aqueous phase than for the organic phase. The split-anion extraction can be applied by using mixtures of ionic liquids. For instance, mixtures of thiocyanate and nitrate ions can be used to extract rare-earths from aqueous solutions with chloride ions. Ionic liquids with perchlorate ions can be used as diluents for thiocyanate and nitrate ionic liquids.



Rare-earth ions cannot be efficiently extracted from chloride or sulfate feed solutions by basic extractants in their chloride or sulfate form. However, the invention shows that rare-earth ions can be extracted from chloride or sulfate feed solutions by basic extractants in their nitrate or thiocyanate form (i.e. by hydrophobic ionic liquids with nitrate or thiocyanate anions), provided that the ionic strength in the aqueous feed solution is sufficiently high. The rare earths are extracted as rare-earth chlorides, rather than rare-earth ions to the organic phase. Because the electrical neutrality is maintained during the extraction process, no ionic liquid components are lost in the aqueous phase due to extraction. In this sense, the extraction mechanism is similar to what is observed for extraction of rare earths by neutral extractants. The rare-earth ions will be coordinated by nitrate or thiocyanate ions in the ionic liquid phase rather than by chloride ions, because of the higher affinity of rare-earth ions for nitrate or thiocyanate ligands compared to chloride ions. The chloride ions remain dissolved in the organic phase, as counter anion for the ionic liquid cations that are not involved as counter cations for the anionic rare-earth complexes. In the ionic liquid phase, anionic rare-earth complexes are formed. If a neutral extractant is added to the ionic liquid phase, it is possible that neutral complexes are formed in the ionic liquid phase, containing the trivalent rare-earth ion, three anions (nitrate or thiocyanate) and one, two or three molecules of the neutral extractant. Increase in the chloride or sulfate concentration leads to an increase in the distribution ratios. It is assumed that the chloride or sulfate salts lower the activity of water, so that less water molecules are available for coordination to the rare-earth ions, so that it is easier to dehydrate the rare-earth ions upon extraction. The extraction process can be carried out by conventional solvent extraction equipment such a mixer-settlers. After extraction, extracted metal ions with low distribution ratios can be scrubbed from the organic phase by an aqueous chloride or sulfate solution. A major advantage of this invention is that stripping from the loaded ionic liquid phase to an aqueous phase is easy, and that it does not require strong mineral acids. It is sufficient to bring the organic phase into contact with water to strip the rare earths as rare-earth chlorides or sulfates to the aqueous phase. A low concentration of salts (for instance 0.1 M ammonium chloride or ammonium sulfate) can be added to the stripping solution to facilitate phase separation of the organic and aqueous phase. The rare earths can be recovered from the stripping solution, for example by precipitation as oxalates with oxalic acid. Calcination of the rare-earth oxalates leads to formation of rare-earth oxides. By stripping the rare-earth chlorides from the ionic liquid phase by pure water, it is possible to obtain aqueous solutions of rare-earth chlorides or sulfates that are not contaminated by other metal chlorides or sulfates. Instead of adding oxalic acid to the aqueous stripping solution containing the rare-earth ions, it is also possible to add solid oxalic acid

to the loaded ionic liquid phase (precipitation stripping). In this way, the rare earths in the ionic liquid phase are transformed in one step to the rare-earth oxalates.

The ionic liquid can be pre-saturated with additional anions ( $A^-$ ) when the ionic liquids are prepared before contact with the aqueous feed solution in order to increase distribution ratios and loading capacity. This is done by contacting the ionic liquid with an aqueous solution containing a salt of the anion in high concentrations which allows the ionic liquid to contain a slightly higher level of the anion. This allows a greater deal of complexation for the extraction. This effect comes directly if the ionic liquid (nitrate or thiocyanate) is prepared from for example a chloride form by contacting it with a concentrated aqueous solution of the corresponding desired ionic liquid anion. The ionic liquids used in the figures and examples are prepared in this pre-saturated form. This slightly increases the level of thiocyanate in the scrub or strip phases.

The selectivity of the extraction process can be tuned by changing the concentration of the chloride or sulfate ions in the aqueous phase, the use of organic complexing agents in the aqueous phase, the type of anion or cation of the ionic liquid used in the organic phase. Quaternary ammonium thiocyanate salts show higher distribution ratios for the LREEs than the quaternary phosphonium thiocyanate salts, but the quaternary phosphonium thiocyanate salts are better extractants for the HREEs than the quaternary ammonium salts. For both quaternary ammonium and phosphonium salts in their thiocyanate form are better extractants for the HREEs than for the LREEs. The use of neutral extractants in combination with the basic extractants (ionic liquids) will lead to a much stronger extraction (higher distribution ratios) for all REEs. The combined use of neutral extractants also allows for much higher loadings of rare earths in the organic phase (in step 1). Prolonged exposure to sunlight and high temperatures leads to some degradation of the thiocyanate ions ( $H_2S$  formation) in thiocyanate ionic liquids. However, no degradation of the ionic liquids was observed (consistent distribution ratios and no  $H_2S$  observed) in samples that were stored in the dark and at room temperature or lower temperatures.

An advantage of this invention is that rare-earths can be extracted from chloride-containing aqueous solutions by basic extractants with different anions, without the need of adding anions other than chlorides to the chloride solution. This also allows for flexibility in the order of the anions in the organic phases that are contacted with the aqueous feed solution. For instance, the HREEs can be extracted from a chloride feed solution by a thiocyanate ionic liquid, leaving the LREEs and yttrium behind in the aqueous phase. By replacing the thiocyanate ionic liquid phase by a nitrate ionic liquid phase, the LREEs can be extracted from the chloride-containing aqueous phase, leaving only yttrium behind. The order of the extractions is not restrictive, i.e. an extraction with

a thiocyanate ionic liquid can be done first, followed by an extraction with a nitrate ionic liquid, or alternatively the extraction with the nitrate ionic liquid can be performed first, followed by an extraction with a thiocyanate ionic liquid. Addition of nitrate or thiocyanate ions to the chloride or sulfate aqueous feed solution is possible, but it will make stripping more difficult since it will be no longer possible to strip the rare earths as pure chloride or sulfate salts, but rather as a mixture of these different anions.

The ionic strength is an important parameter in these solvent extraction processes. First of all, the chloride or sulfate concentration has an influence on the distribution ratios during the initial solvent extraction process. The ionic strength also has an influence on the scrubbing and stripping steps. It is possible to change the distribution ratios by changing the concentration of the chloride or sulfate salts in the aqueous solutions. The aqueous phase can be sequentially contacted with different batches of the organic phase and between the different contacts the chloride or sulfate concentration in the aqueous phase is gradually increased by dissolution of extra chloride or sulfate salts. In an extraction process with thiocyanate ionic liquids, first the HREEs are extracted. Between each step of increased ionic strength a contact with either, thiocyanate- or nitrate-based ionic liquids can be performed or with both types sequentially. By increasing the chloride or sulfate concentration of the aqueous solution, gradually additional rare earths are extracted in each step. In principle, this approach can be used to sequentially extract the rare earths from the aqueous solution, starting from lutetium and gradually moving towards lanthanum for thiocyanate-based ionic liquids and the reverse for nitrate-based ionic liquids (though separation factors are lower for nitrate-based extraction).

Whereas it is possible to strip most of the extracted rare earths in one step from the loaded organic phase by water or by an aqueous solution containing low concentrations of dissolved salts (e.g. 0.1 M ammonium chloride or 0.1 M ammonium sulfate) to facilitate the separation of the two phases after stripping, it is also possible to selectively strip some of the rare earths dissolved in the organic phase. The selective stripping can be achieved by using different concentrations of dissolved chloride or sulfate salts, with or without adding a complexing agent such as EDTA. Selective stripping from an organic phase containing a nitrate ionic liquid is also possible by using aqueous solutions with different concentrations of nitrate ions, with or without adding a complexing agent such as EDTA.

A person skilled in the art will understand that large variations in the rare-earth composition of the aqueous feed solutions are possible, because the rare-earth concentrates can originate from different sources. For instance, rare-earth concentrates prepared from different rare-earth ores or even from the same rare-earth ore but from

different geographical locations which have different contents of the individual rare earths. Also rare-earth concentrates obtained from activities related to the recycling of rare earths from end-of-life consumer goods will have compositions that are very different from those obtained from rare-earth ores. In particular, the ratios between LREEs and HREEs can be quite different in the different concentrates. In order to have the most efficient extraction, the extraction parameters need to be optimized for each different aqueous feed solution, a process within the normal skills of the skilled-in-the-art person. Process parameters that need to be adjusted are the ionic strength (salt concentration) of the feed solution, rare earth concentrations, the concentration of potential complexing agents in the aqueous feed solution, the phase volume ratios (flow rates), the composition of organic phase (only basic extractants, or basic extractants combined with neutral extractants) and optimal temperatures for different stages.

The split-anion extraction can be used for the preprocessing of rare-earth concentrates. The preprocessing can include removal of rare earths from other metallic elements present in the acidic leaching solution, but the method can also be used for the removal of lanthanum and/or cerium from rare-earth concentrates. Lanthanum and cerium are often abundant in rare-earth concentrates, but they have a low intrinsic value compared to the other rare earths. Removal of lanthanum and/or cerium in a preprocessing step can lead to a rare-earth concentrate with a higher added value.

The split-anion extraction with extraction from chloride aqueous solutions by nitrate or thiocyanate ionic liquids is very efficient for the extraction of scandium. As such, the split-anion extraction is useful for the recovery of scandium together with the other rare earths from acidic leach solutions of bauxite residue (red mud). The leachate can contain many elements other than the rare earths and scandium, often in larger concentration than the targeted metal ions (e.g. iron, aluminium, titanium). Therefore, the recovery process consists of different consecutive extraction, scrubbing (washing) and stripping steps, depending on the metals and anions present. In a typical process, a  $\text{H}_2\text{SO}_4$  or  $\text{HCl}$  leachate obtained by selective leaching of bauxite residue is contacted with the ionic liquid trihexyl(tetradecyl)phosphonium nitrate containing TBP. This organic phase will extract scandium, other rare earths and part of the iron from the aqueous phase. A scrub of the ionic liquid phase with a concentrated nitrate salt solution will remove a large part of the co-extracted iron. The rare earths can be stripped from the ionic liquid phase by a  $\text{HCl}$ ,  $\text{HNO}_3$  or  $\text{H}_2\text{SO}_4$  solution. From this aqueous solution the rare earths can be separated. For instance, scandium can be removed by a thiocyanate ionic liquid and the other rare earths can be removed by a nitrate ionic liquid. The possibility of using in a consecutive way a chloride, thiocyanate and nitrate ionic liquid without the

need of adjusting the composition of the aqueous phase is one of the strengths of the split-anion approach.

The split-anion extraction has also applications in the recycling of rare earths. In the recycling of nickel-metal hydride batteries, the rare earths can be extracted as a group from the nickel by an organic phase containing a nitrate or thiocyanate ionic liquid, after dissolution of the mixed electrodes in hydrochloric acid. Neodymium and other rare earths can be recovered from neodymium magnets after dissolution of the magnets in hydrochloric acid or sulfuric acid, followed by extraction with a nitrate or thiocyanate ionic liquid. Rare earths can be recovered from lamp phosphors by extraction with an organic phase containing nitrate or thiocyanate ions after dissolution of the lamp phosphors in hydrochloric acid or sulfuric acid.

The application of split-anion extraction is not restricted to the use of conventional liquid-liquid extraction (solvent extraction processes), but it can be used in extraction chromatography as well. In extraction chromatography, the ionic liquid phase is immobilized on a high-surface area solid support by impregnation (supported ionic liquid phases or SILPs). The SILPs combine the advantages of ionic liquid solvent extraction systems and ion-exchange resins, and are very useful for the recovery of metals from diluted aqueous streams. Examples of solid supports are silica, alumina, activated carbon, or porous synthetic polymer resins such as polystyrene cross-linked by divinylbenzene.

## BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1: Distribution ratios for two separate mixtures of rare earths at approximately 0.02 M each in a 4 M magnesium chloride matrix when contacted with the organic phases based on trihexyl(tetradecyl)phosphonium nitrate and trihexyl(tetradecyl)phosphonium thiocyanate, scandium was fully extracted.

Figure 2: Distribution ratios for two separate mixtures of rare earths at approximately 0.02 M each in a 4 M magnesium chloride matrix when contacted with the organic phases based on tricaprylmethylammonium nitrate and tricaprylmethylammonium thiocyanate, scandium was fully extracted.

Figure 3: Distribution ratio variations depending on chloride concentrations (2 – 8 M) for the initial step of extractions using trihexyl(tetradecyl)phosphonium thiocyanate on a HREE rich (approximately 50%) rare-earth mixture made based on the composition of an eudialyte ore. The distribution ratios for yttrium are shown to the right.

Figure 4: Distribution ratio variations depending on chloride concentrations (2 – 8 M) for the initial step of extractions using trihexyl(tetradecyl)phosphonium thiocyanate on a rare earth mixture with approximately 15% HREE. The distribution ratios for yttrium are shown to the right.

Figure 5: Distribution ratio variations depending on chloride concentrations (4 – 8 M) for an initial extraction step using trihexyl(tetradecyl)phosphonium nitrate on a HREE rich (approximately 50%) rare earth mixture made based on the composition of an eudialyte ore. The distribution ratios for yttrium are shown to the right.

Figure 6: Distribution ratio variations depending on chloride concentrations (4 – 8 M) for an initial extraction step of using trihexyl(tetradecyl)phosphonium nitrate on a rare earth mixture with approximately 15% HREE. The distribution ratios for yttrium are shown to the right.

Figure 7: Effect of added neutral extractant (Cyanex 923) on distribution ratios for a low rare earth concentration (approximately 0.001 M of each rare earth) in 4 M calcium chloride ( $\text{CaCl}_2$ ).

Figure 8: A scheme for metal recovery from nickel metal hydride batteries (mixed electrodes) dissolved in hydrochloric acid. A small amount of neutral extractant can be used to raise distribution ratios (0-15% is sufficient for 8 M chloride aqueous solutions).

## EXAMPLES

### EXAMPLE 1. Synthesis of ionic liquids.

Trihexyl(tetradecyl)phosphonium thiocyanate and tricaprylmethylammonium thiocyanate were prepared from the corresponding chloride ionic liquids by pre-equilibrating the chloride ionic liquids two times with a 3 M  $\text{NH}_4\text{SCN}$  solution to exchange the chloride ions for thiocyanate ions. This gave water-saturated thiocyanate ionic liquids.

Trihexyl(tetradecyl)phosphonium nitrate and tricaprylmethylammonium nitrate were prepared from the corresponding chloride ionic liquids by pre-equilibrating the chloride ionic liquids two times with a 2.5 M  $\text{KNO}_3$  solution to exchange the chloride ions for nitrate ions. Trihexyl(tetradecyl)phosphonium perchlorate was prepared from trihexyl(tetradecyl)phosphonium chloride by pre-equilibrating the chloride ionic liquid three times with a 2 M  $\text{NaClO}_4$  solution to exchange the chloride ions for perchlorate ions, followed by washing with pure water.

## EXAMPLE 2. Separation factors over the rare-earth group using thiocyanate ionic liquids

All separation factors between rare earths were determined between two equimolar aqueous solutions with a 8 M chloride matrix (4 M  $\text{MgCl}_2$ ) and thiocyanate ionic liquid phases (trihexyl(tetradecyl)phosphonium thiocyanate, tricaprylmethylammonium thiocyanate). The two rare-earth solutions each contained half the rare earths each at approximately 0.02 M individual metal concentration. The extractions were carried out at 50 °C with a phase ratio of 1:1 and mixed until equilibrium conditions were reached. The obtained separation factors are listed in Table 1 for trihexyl(tetradecyl)phosphonium thiocyanate and Table 2 tricaprylmethylammonium thiocyanate. The distribution ratios for these experiments are also shown in Figures 1 and 2.

Table 1.

	Yb	Tm	Er	Ho	Dy	Y	Tb	Gd	Eu	Sm	Nd	Pr	Ce	La
Lu	3.2	20	40	100	190	450	450	1600	1900	3300	13000	25500	41500	208000
	Yb	6.5	12	30	59	140	140	500	590	1036	4000	7900	12900	64500
		Tm	1.9	4.6	9	21	21	78	91	160	630	1200	2000	10000
			Er	2.4	5	11	11	41	48	84	330	640	1000	5200
				Ho	2.0	4.6	4.6	17	20	35	140	270	430	2200
					Dy	2.4	2.4	8.6	10	18	69	140	220	1100
						Y	1.0	3.7	4.3	8	29	57	93	470
							Tb	3.7	4.3	7.5	29	57	93	470
								Gd	1.2	2.0	8.0	16	25	130
									Eu	1.8	6.9	14	22	110
										Sm	3.9	7.6	12	62
											Nd	1.9	3.2	8.2
												Pr	1.6	8.2
													Ce	5.0

Table 2

	Yb	Tm	Er	Ho	Dy	Tb	Gd	Eu	Y	Sm	Nd	Pr	Ce	La
Lu	2.5	6	16	35	43	90	180	240	310	350	1300	2100	1750	13000
	Yb	2.3	6.4	14	17	36	73	96	126	140	540	860	700	5200
		Tm	2.7	6.0	7.4	15	31	41	54	60	231	370	300	2200
			Er	2.2	2.7	5.7	11	15	20	22	85	135	110	820
				Ho	1.2	2.6	5.1	6.8	8.9	10	38	61	50	370
					Dy	2.1	4.2	5.5	7.3	8	31	50	41	300
						Tb	2.0	2.7	3.5	4	15	24	20	150
							Gd	1.3	1.7	1.9	7.5	12	9.7	72
								Eu	1.3	1.5	5.7	9.0	7.4	55
									Y	1.1	4.3	6.8	5.6	41
										Sm	3.9	6.1	5.0	37
											Nd	1.6	1.3	6.0
												Pr	0.8	6.0
													Ce	7.4

It was found that especially the trihexyl(tetradecyl)phosphonium thiocyanate had large separation factors over the entire series of rare earths due to the low extraction of light rare earths and is therefore suitable for solvent extraction separation of rare earths. Both ionic liquids extracted scandium to below detection limits in the aqueous phase.

### EXAMPLE 3. Separation factors over the rare-earth group using nitrate ionic liquids

All separation factors between rare earths were determined between two equimolar aqueous solutions with a 8 M chloride matrix (4 M  $\text{MgCl}_2$ ) and nitrate ionic liquid phases (trihexyl(tetradecyl)phosphonium nitrate, tricaprylmethylammonium nitrate). The two rare earth solutions each contained half the rare earths each at approximately 0.02 M individual metal concentration. The extractions were carried out at 50 °C with a phase ratio of 1:1 and mixed until equilibrium conditions were reached. The obtained separation factors are listed in Table 3 for trihexyl(tetradecyl)phosphonium nitrate and Table 4 tricaprylmethylammonium nitrate. The distribution ratios for these experiments are also shown in Figures 1 and 2.

Table 3

	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Y	Lu
La	0.6	1	0.9	1.6	2.0	2.7	4.8	3.3	8	7	18	20	30	46
	Ce	2.4	1.5	2.8	3	4	8	6	13	12	30	34	50	77
		Pr	0.7	1.2	1.4	1.9	3	2.4	6	5	13	14	21	33
			Nd	1.8	2.2	2.9	5	3.6	9	8	20	22	33	50
				Sm	1.2	1.6	2.9	2.0	4.8	4.3	11	12	18	28
					Eu	1.3	2.4	1.6	3.9	3.5	9	10	15	23
						Gd	1.8	1.2	3.0	2.6	7	8	11	17
							Tb	0.7	1.6	1.5	3.7	4.2	6	9
								Dy	2.4	2.1	5.4	6.1	9	14
									Ho	0.9	2.2	2.5	4	6
										Er	2.5	2.9	4	7
											Tm	1.1	1.7	2.3
												Yb	1.5	2.3
													Y	1.5

Table 4

	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Y	Lu
La	0.2	1	0.7	2.4	1.6	3	4	3	5	7	21	18	25	43
	Ce	4.9	3.5	12.5	8	16	19	18	28	35	110	97	130	230
		Pr	0.7	2.5	2	3	4	4	6	7	23	20	27	46
			Nd	3.6	2.4	4.5	5	5.1	8	10	32	28	38	65
				Sm	0.7	1.3	1.5	1.4	2.2	2.8	9	8	11	18
					Eu	1.9	2.2	2.1	3.3	4.2	14	12	16	27
						Gd	1.2	1.1	1.8	2.2	7	6	9	14
							Tb	1.0	1.5	1.9	6.0	5.2	7	12
								Dy	1.6	2.0	6.3	6	8	13
									Ho	1.3	4.1	3.5	5	8
										Er	3.2	2.8	4	7
											Tm	0.9	1.2	2.3
												Yb	1.4	2.3
													Y	1.7

It was found that both the nitrate ionic liquids were capable of rare earth extraction and separation from a chloride media with high distribution ratios over the entire series. The preference is for light rare earths unlike the thiocyanate-based ionic liquids. The nitrate-



based ionic liquids are therefore suitable for solvent extraction separation of rare earths. Both ionic liquids extracted scandium to below detection limits in the aqueous phase.

**EXAMPLE 4. Dependence on chloride concentration for trihexyl(tetradecyl)phosphonium thiocyanate extractions for a 50% HREE feed in chloride media**

The chloride matrix effect on extraction with trihexyl(tetradecyl)phosphonium thiocyanate is shown in Figure 3 by varying the concentration between 2 and 8 M chloride ( $\text{MgCl}_2$ ) on a HREE rich (approximately 50%) rare-earth mixture made based on the composition of an eudialyte ore. The loading of the organic phase for the highest chloride concentration is approximately 15 g/L.

The conclusion to be drawn is that a high chloride concentration is necessary to achieve significant extraction of multiple HREEs, but that the heavier elements can still be extracted at less than 8 M chloride concentration.

**EXAMPLE 5. Dependence on chloride concentration for trihexyl(tetradecyl)phosphonium thiocyanate extractions for a 15% HREE feed in chloride media**

In the same way as in example 3, example 4 shows the effect of chloride concentration, with a different aqueous feed solution where the HREE content is reduced from 50% of rare earths to 15%. The chloride matrix effect on extraction with trihexyl(tetradecyl)phosphonium thiocyanate is shown in Figure 4 by varying the concentration between 2 and 8 M chloride ( $\text{MgCl}_2$ ) on a less HREE rich (approximately 15%) rare earth mixture. The loading of the organic phase for the highest chloride concentration is approximately 10 g/L.

The conclusion to be drawn is that the optimal value differs from that of Example 3 and is therefore dependent on composition when optimizing chloride content.

**EXAMPLE 6. Dependence on chloride concentration for trihexyl(tetradecyl)phosphonium nitrate extractions from a 50% HREE feed in chloride media**

The chloride matrix effect on extraction from a feed solution with trihexyl(tetradecyl)phosphonium nitrate is shown in Figure 5 by varying the concentration between 4 and 8 M chloride ( $\text{MgCl}_2$ ) on a HREE rich (approximately 50%) rare earth mixture made based on the composition of an eudialyte ore. The loading of the organic phase for the highest chloride concentration is approximately 30 g/L.

The conclusion to be drawn is that for the nitrate ionic liquids a high chloride concentration is necessary to achieve significant extraction of LREEs. The distribution ratios are clearly lower than displayed in Figure 1, which is an effect of the higher loading of the organic phase and is therefore dependent on composition when optimizing chloride content.

**EXAMPLE 7. Dependence on chloride concentration for trihexyl(tetradecyl)phosphonium nitrate extractions for a 15% HREE feed in chloride media**

In the same way as in Example 6, Example 7 shows the effect of chloride concentration, with a different aqueous feed solution where the HREE content is 15%. The chloride matrix effect on extraction with trihexyl(tetradecyl)phosphonium nitrate is shown in Figure 6 by varying the concentration between 4 and 8 M chloride ( $\text{MgCl}_2$ ) on the rare earth mixture. The loading of the organic phase for the highest chloride concentration is approximately 40 g/L.

The distribution ratios are clearly lower than displayed in Figure 1, which is an effect of the higher loading of the organic phase and is therefore dependent on composition when optimizing chloride content.

**EXAMPLE 8. Effect of neutral extractant Cyanex 923 on distribution ratios**

The effect of neutral extractants on the distribution ratios of extraction from an 8 M chloride matrix with a mixture of 0.001 M of each rare earth added is illustrated in Figure 5. The distribution ratios are significantly increased by the addition of Cyanex 923. For example at above 10% (v/v) addition of Cyanex 923 the distribution ratios exceed 100 for gadolinium and the elements further in the lanthanide series. This also allows for lowered chloride levels in the feed if desired and thereby offering a greater versatility when optimizing selectivity by chloride addition.

**EXAMPLE 9. Split-anion application on other metals (nickel metal hydride battery recycling)**

Applying split-anion extraction to rare earths together with other metals is demonstrated using tricaprylmethylammonium nitrate to extract metals from a chloride-based solution mimicking a dissolved nickel metal hydride battery, at 8 M chloride concentration, gave the distribution ratios found in Table 5. Adding a neutral extractant, in the form of 15 % (v/v) Cyanex 923, to the solvent resulted in fully extracted zinc and the rare earths and giving the distribution ratios found in Table 6 for the remaining metals.

Table 5

Co	Fe	Mn	Ni	Zn	Y	La	Ce	Pr	Nd
19	4.0	3.1	0.01	>100	0.3	28	34	3.7	2.0

Table 6

Co	Fe	Mn	Ni
36	7.4	4.2	0.01

The resulting loaded ionic liquid is subsequently scrubbed with a solution with a high concentration of chloride ions (for example 4 M  $\text{MgCl}_2$ ). The first strip step is done with a nitrate solution, stripping cobalt and manganese. The second strip step strips the lanthanides using a hydrochloric acid solution and finally the zinc and iron is cleaned from the ionic liquid using water, nitric acid or ammonia. A scheme for this separation is shown in Figure 8. The transition metals (Co, Fe, Mn, Zn), except nickel, can also be pre-extracted from the original aqueous chloride liquor using a chloride ionic liquid such as Aliquat 336 or Cyphos IL 101.

#### EXAMPLE 10. Stripping of tricaprylmethylammonium thiocyanate

Stripping tricaprylmethylammonium thiocyanate loaded with a small amount of rare earths is demonstrated in Table 7 using 4, 2 and 0 M  $\text{MgCl}_2$  solutions. The large difference in distribution ratios exemplifies the ability to strip selectively.

Table 7. Distribution ratios for tricaprylmethylammonium thiocyanate ( $[\text{A336}][\text{SCN}]$ ) when contacted with three metal-free aqueous phases with varying chloride concentrations.

	4 M $\text{MgCl}_2$	2 M $\text{MgCl}_2$	Water
La	0.5	0.03	0.003
Ce	1.9	0.06	0.003
Pr	5.4	0.17	0.007
Nd	8.5	0.19	0.01
Sm	61	0.95	0.03
Eu	91	1.1	0.04
Gd	79	1.4	0.04
Tb	90	0.61	0.04
Dy	28	0.11	0.001
Ho	210	1.0	0.06
Er	64	0.17	0.0004
Tm	960	2.6	0.15

Yb	460	0.66	0.00093
Lu	>1000	12	0.61
Y	4	0.002	<0.001

### EXAMPLE 11. Stripping of trihexyl(tetradecyl)phosphonium thiocyanate

Stripping trihexyl(tetradecyl)phosphonium thiocyanate loaded with a small amount of rare earths is demonstrated in Table 8 using 4, 2 and 0 M MgCl<sub>2</sub> solutions. The large difference in distribution ratios exemplifies the ability to strip selectively.

Table 8. Distribution ratios for strip of rare earths in trihexyl(tetradecyl)phosphonium thiocyanate when contacted with three metal-free aqueous phases with varying chloride concentrations.

	4 M MgCl <sub>2</sub>	2 M MgCl <sub>2</sub>	Water
La	0.0	<0.001	<0.001
Ce	0.2	0.02	<0.001
Pr	0.5	0.06	0.012
Nd	0.6	0.06	0.01
Sm	3	0.28	0.06
Eu	5	0.3	0.07
Gd	6	0.4	0.07
Tb	4	0.04	0.01
Dy	2	0.03	0.012
Ho	17	0.1	0.03
Er	7	0.07	0.0015
Tm	142	1.0	0.22
Yb	65	0.70	0.01200
Lu	1050	7	1.61
Y	1	<0.001	<0.001

### EXAMPLE 12. Dependence of the extraction on the pH

The trend of pH dependence is similar over the different elements, but varies with the chloride concentration. The pH dependence is such that at above pH 1.5–2 the distribution ratios are fairly constant for the 8 M chloride solution and in more acidic conditions (pH < 1.5) the distribution ratios fall rapidly. For the solution with the lower chloride concentration (4 M) the distribution ratios are low at low pH but increases linearly with an increasing pH value.

### EXAMPLE 13. Kinetic experiments

The kinetics of extraction with tricaprylmethylammonium thiocyanate and trihexyl(tetradecyl)phosphonium thiocyanate were studied using an aqueous solution

with a chloride matrix (4 M  $\text{MgCl}_2$ ), spiked with ytterbium(III) chloride to approximately 30 g/L. The experiments were carried out at 30 °C with a phase ratio of 1:1 and high mixing speed (3000 rpm). Samples were centrifuged for 30 s and the phases were separated immediately after. The time required to reach equilibrium for both the thiocyanate ionic liquid systems was approximately 10 to 12 min. The equilibration time can be influenced by, for example, changing the mixing speed or the temperature.

#### **EXAMPLE 14. Loading experiments**

The organic phase loading capacity for individual metals in the thiocyanate ionic liquids is approximately 0.14–0.26 mol/L (depending on the individual metal). The loading capacity of tricaprylmethylammonium thiocyanate (0.26 mol/L or 46 g/L for ytterbium) is higher than for trihexyl(tetradecyl)phosphonium thiocyanate, but was of the same order of magnitude. The influence of loading is very high since there can be a difference of a factor of approximately 10000 in distribution ratio between an aqueous loading of 0.0001 M and 1 M. This means that optimization with respect to loading is very important for process development. Tricaprylmethylammonium thiocyanate displays a very similar loading behavior for single elements, but with slightly higher loading capacity.

#### **EXAMPLE 15. Dependence of extraction on thiocyanate ion**

To study the extraction behaviour without losing the ionic liquid character of the organic phase, an ionic liquid with anions not forming extractable complexes with rare-earth ions was required. Since perchlorate ions have low tendencies to form such complexes and a higher tendency to reside in the ionic liquid than chloride anions, the ionic liquid trihexyl(tetradecyl)phosphonium perchlorate was found to be excellent for this purpose. Dysprosium extraction into pure trihexyl(tetradecyl)phosphonium perchlorate was investigated with varying amounts of thiocyanate added to the initial 6 M chloride aqueous phase. The slope of the distribution ratios versus the thiocyanate concentration (log-log) is equivalent to the number of thiocyanate anions required to extract from the aqueous phase. The obtained slope was 3.2, which indicates that the distribution ratio of the rare earths will vary with the thiocyanate concentration in the aqueous phase to the power of three. In an equivalent experiment using trihexyl(tetradecyl)phosphonium thiocyanate (washed) instead of trihexyl(tetradecyl)phosphonium perchlorate, the slope of the log-log plot was 3.05, also indicating that three thiocyanate anions are required to extract from the aqueous phase. Using the information gained by varying the thiocyanate concentration with trihexyl(tetradecyl)phosphonium perchlorate showed that 0.295 M thiocyanate added to the aqueous phase gave the same distribution ratio as pure trihexyl(tetradecyl)phosphonium thiocyanate (washed) for 50 mM dysprosium in 6 M chloride solutions. This is much lower than the approximately 1.6 M thiocyanate (depending on water-saturation levels) present in pure trihexyl(tetradecyl)phosphonium

thiocyanate. This large difference indicates that a large part of the perchlorate anions remain in the ionic liquid, thereby increasing the free thiocyanate concentration available to complex with the rare earth ions. This could be utilized to reduce the level of thiocyanate in the ionic liquid while maintaining high distribution ratios.

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B. Gaudernack, G. Hannestad, I. Hundere, "Process for separation of yttrium from the lanthanides", US Patent 3,821,352 (1974).

**CLAIMS**

1. A process for removing with an extraction method one or more rare-earth elements from a hydrophilic composition, the process comprising the steps of
  - providing a hydrophilic composition comprising one or more rare-earth elements and one or more rare earth complexing  $B^-$  anions
  - separating one or more rare-earth element from said solution by extraction with a water-immiscible organic phase comprising an ionic liquid with one or more rare earth element complexing  $A^-$  anions,  
wherein the  $A^-$  anion in the water-immiscible organic phase is an anion with a lower hydrophylicity than the  $B^-$  anion in the hydrophilic composition.
2. The process according to claim 1, wherein the one or more  $B^-$  anions are selected from the group consisting of chloride, sulfate and nitrate.
3. The process according to claim 1 or 2, wherein the one or more  $A^-$  anions are nitrate or thiocyanate.
4. The process according to any one of claims 1 to 3, wherein the  $B^-$  anion is chloride and the  $A^-$  anion is nitrate.
5. The process according any one of claims 1 to 4, wherein the hydrophilic composition is an aqueous solution.
6. The process according to anyone of claims 1 to 4, wherein the hydrophilic composition is a molten salt phase, a molten salt hydrate phase or an ionic liquid phase, wherein these phases are immiscible with the organic phase.
7. The process according to any one of claims 1 to 6, wherein the organic phase is immobilized or impregnated on a solid support.
8. The process according to any one of claims 1 to 7, wherein the organic phase comprises an ionic liquid selected from the group consisting of tricaprilmethylammonium nitrate, tricaprilmethylammonium thiocyanate, trihexyl(tetradecyl)phosphonium nitrate and trihexyl(tetradecyl)phosphonium thiocyanate.

9. The process according to any one of claims 1 to 8, wherein a neutral extractant has been dissolved in the organic phase. BE2015
10. The process according to claim 9, wherein the neutral extractant is tri-*n*-butylphosphate (TBP), or is a mixture of tri(*n*-hexyl)phosphine oxide and tri(*n*-octyl)phosphine oxide (Cyanex 923), or is a mixture of bis(2,4,4-trimethylpentyl) *n*-octylphosphine oxide and tris(2,4,4-trimethylpentyl)phosphine oxide (Cyanex 925).
11. The process according to any one of claims 1 to 10, wherein the organic phase further comprises a diluent.
12. The process according to any one of claims 1 to 11, wherein a water-soluble complexing agent is added to the hydrophilic composition.
13. The process according to any one of claims 1 to 12, wherein the hydrophilic composition is repeatedly extracted with organic phase.
14. The process according to claim 13, wherein the hydrophilic composition is sequentially, and at least twice, extracted with organic phases of a different composition.
15. The process according to claim 13 or 14, wherein the concentration of anion B<sup>-</sup> in the hydrophilic composition is varied in the individual extractions, for example by dissolution of salts containing anion B<sup>-</sup> or by dilution.
16. The process according to 15, wherein the concentration of anion B<sup>-</sup> is increased by addition of a compound selected from the group consisting of calcium chloride, magnesium chloride, nickel(II) chloride, lithium chloride, ammonium chloride, a mixture of lithium- and ammonium-chloride, and ammonium sulfate .
17. The process according to claim 13 or 14, which is a continuous process wherein the concentration of anion B<sup>-</sup> in the hydrophilic composition is continuously increased or decreased, for example by respectively the dissolution of salts containing anion B<sup>-</sup> or dilution with water.
18. The process according to any of claims 13 to 15, which is at least a two-step process, wherein the hydrophilic composition is sequentially contacted with the



organic phase, wherein at least in one step a different concentration of anion  $B^-$  is used in the hydrophilic composition. <sup>BE2015</sup>

19. The process according to any one of claims 1 to 11, wherein yttrium is separated from the other rare-earth elements, which is at least a two-step process, wherein the hydrophilic composition comprising chloride anions as  $B^-$  anions is contacted with an organic phase comprising an ionic liquid and nitrate anions as  $B^-$  anions, followed by a second contact of the hydrophilic composition with an organic phase comprising an ionic liquid and thiocyanate anions as  $B^-$  anions, whereby the yttrium remains in the hydrophilic composition and the other rare-earth elements are extracted to the organic phases.
20. The process according to claim 18, wherein the aqueous phase is first extracted with an organic phase wherein  $A^-$  is nitrate, followed by a second extraction with an organic phase wherein  $A^-$  is thiocyanate.
21. The process according to claim 18, wherein the aqueous phase is first extracted with an organic phase wherein  $A^-$  is thiocyanate, followed by a second extraction with an organic phase wherein  $A^-$  is nitrate.
22. The process according to any one of claims 1 to 21, further comprising the step of selectively or complete isolating rare-earth elements from the organic phase by stripping with water or with an aqueous phase comprising a rare earth complexing anion  $B^-$  in a concentration that is lower compared to the  $B^-$  anion concentration in the hydrophilic composition before extration.
23. The process according to claim 22, wherein the  $B^-$  anion in the stripping solution is the same anion as the  $B^-$  anion in the hydrophilic composition before extraction, for example said  $B^-$  anion is chloride.
24. Use of an ionic liquid with rare-earth element complexing anions to remove one or more rare earth elements from a hydrophilic composition, by contacting said hydrophilic composition, comprising one or more rare-earth elements and one or more rare earth complexing  $B^-$  anions, with a water-immiscible organic phase, comprising said ionic liquid with one or more rare earth element complexing  $A^-$  anions, wherein the  $A^-$  anion in the water-immiscible organic phase is an anion with a lower hydrophylicity than the  $B^-$  anion in the hydrophilic composition.

## FIGURES

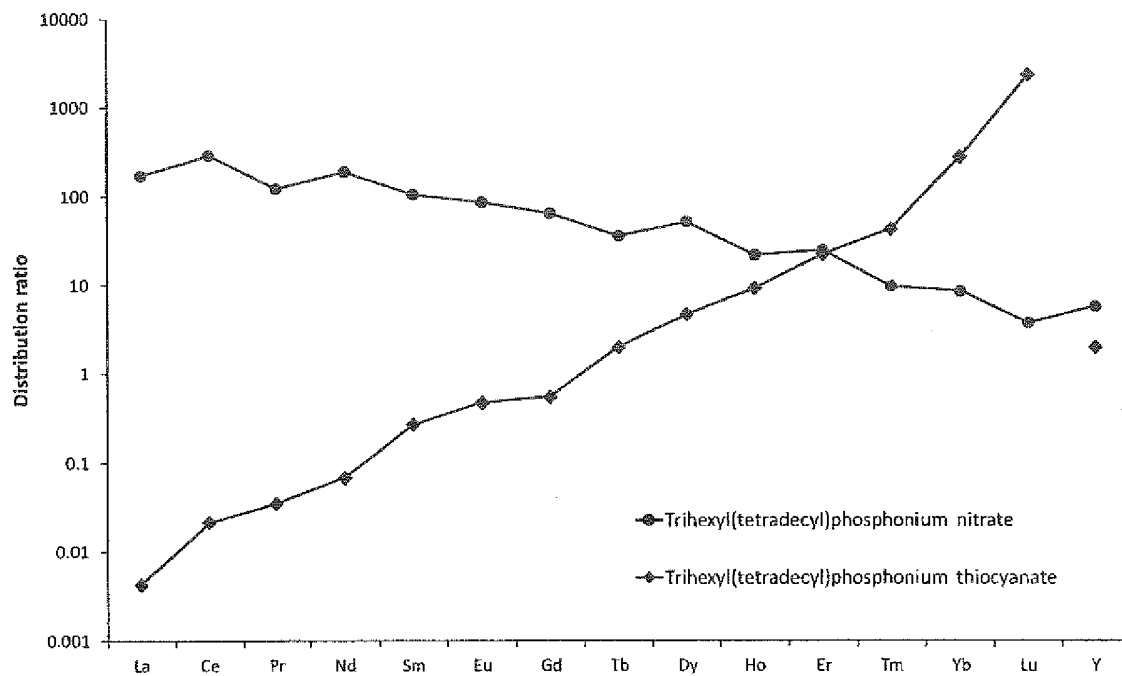


Figure 1.

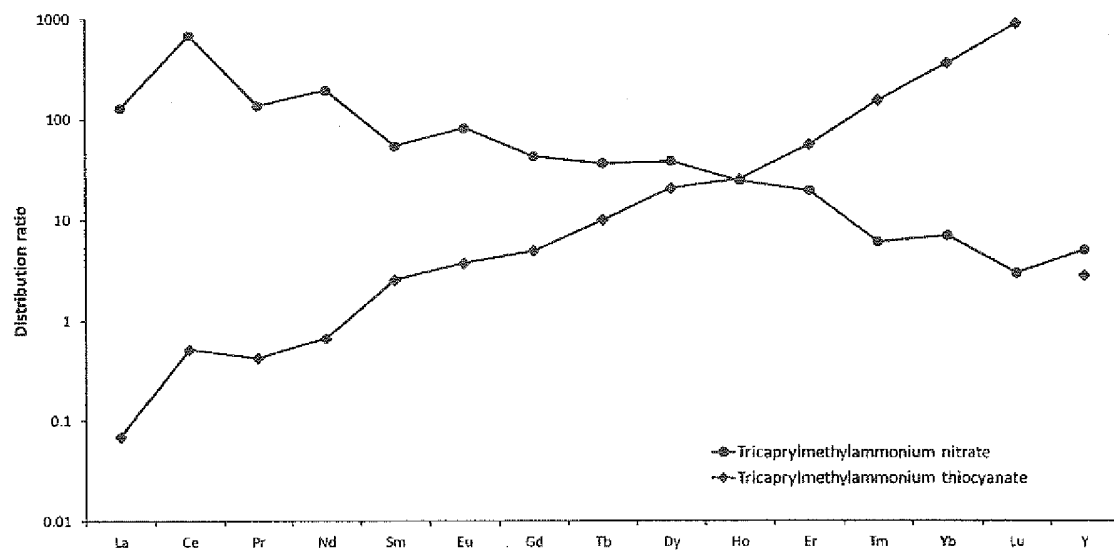


Figure 2.

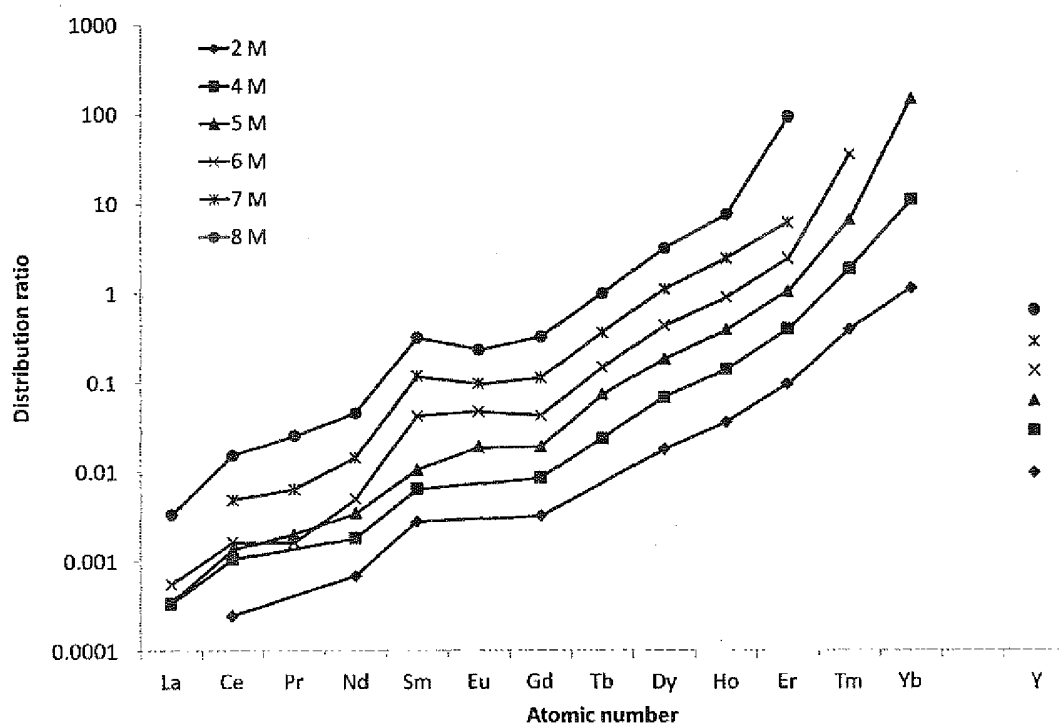


Figure 3.

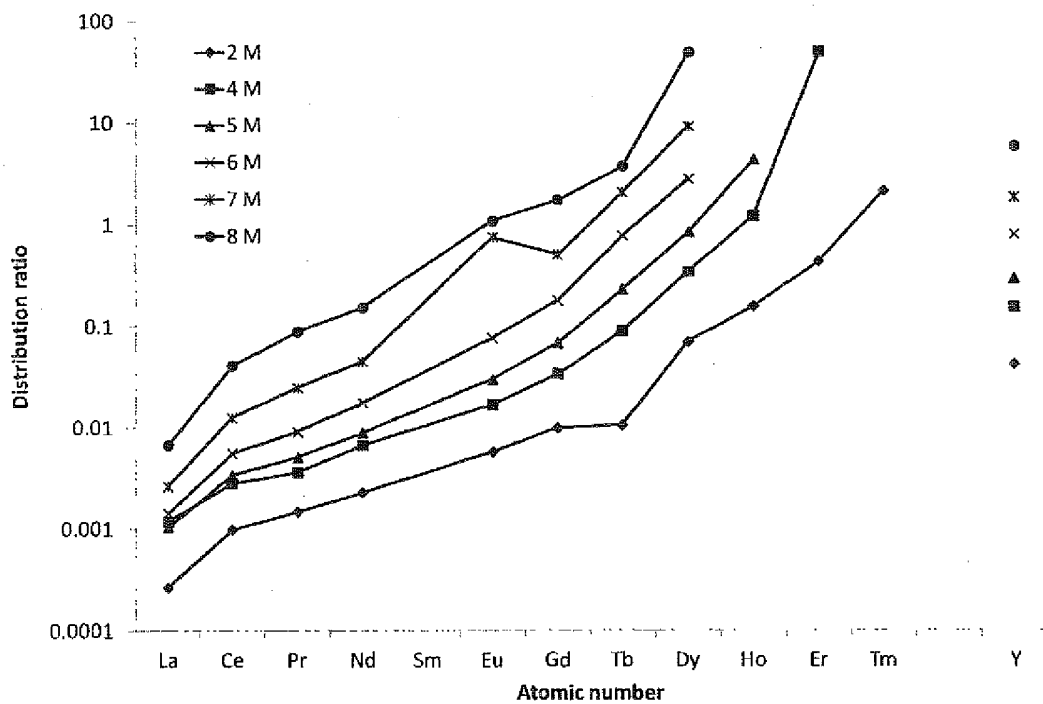


Figure 4.

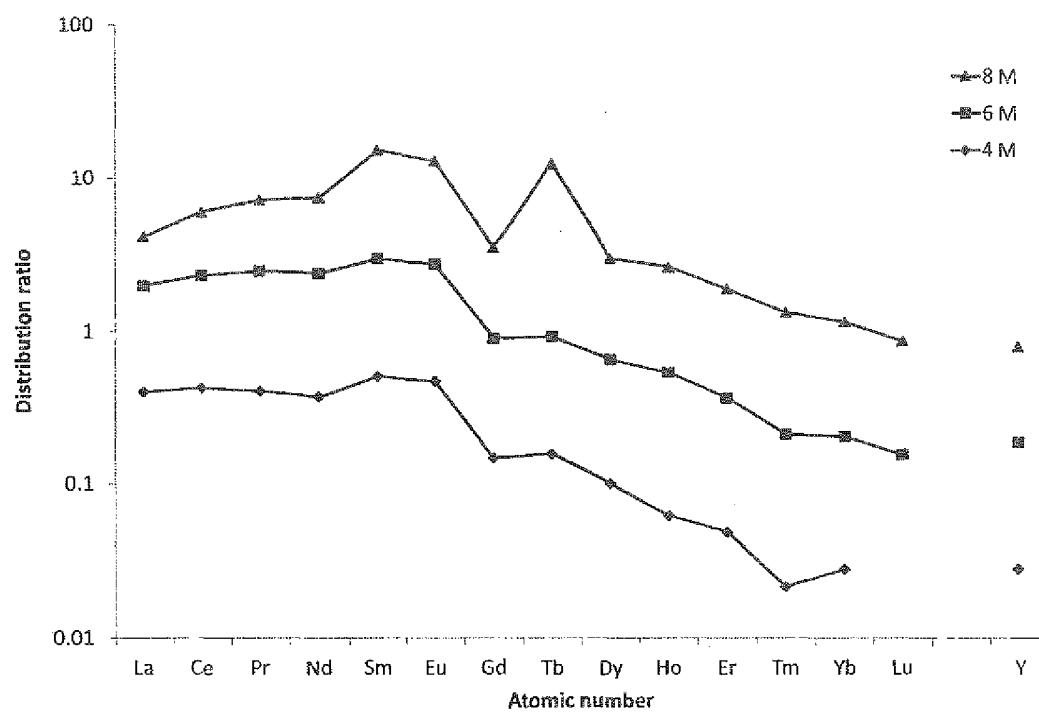


Figure 5.

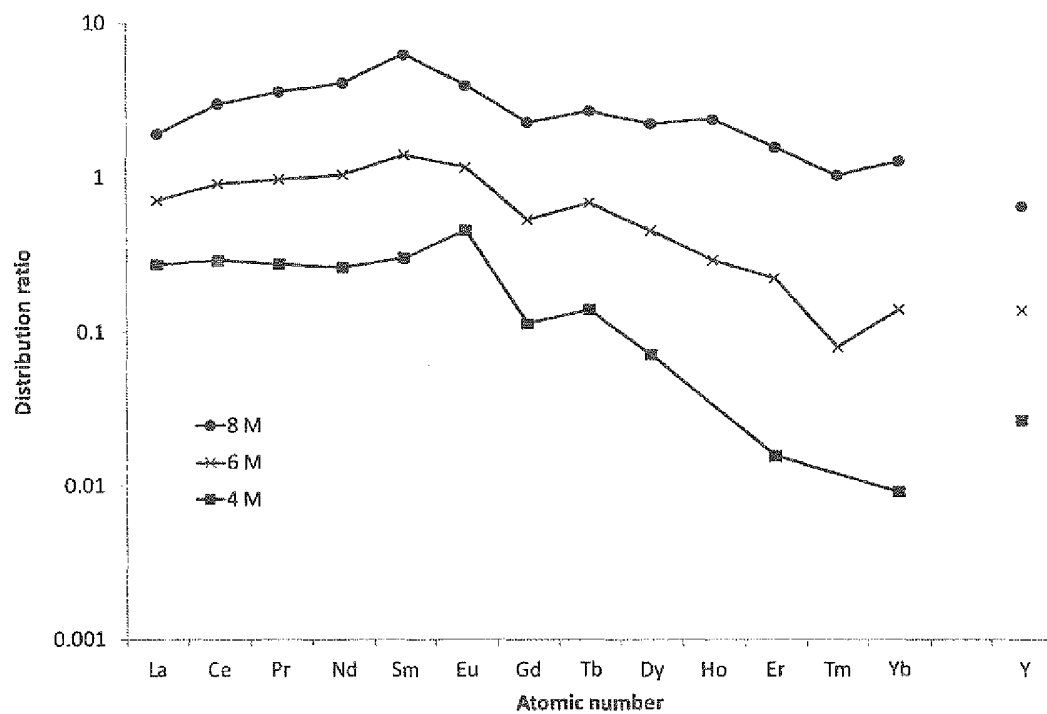


Figure 6.

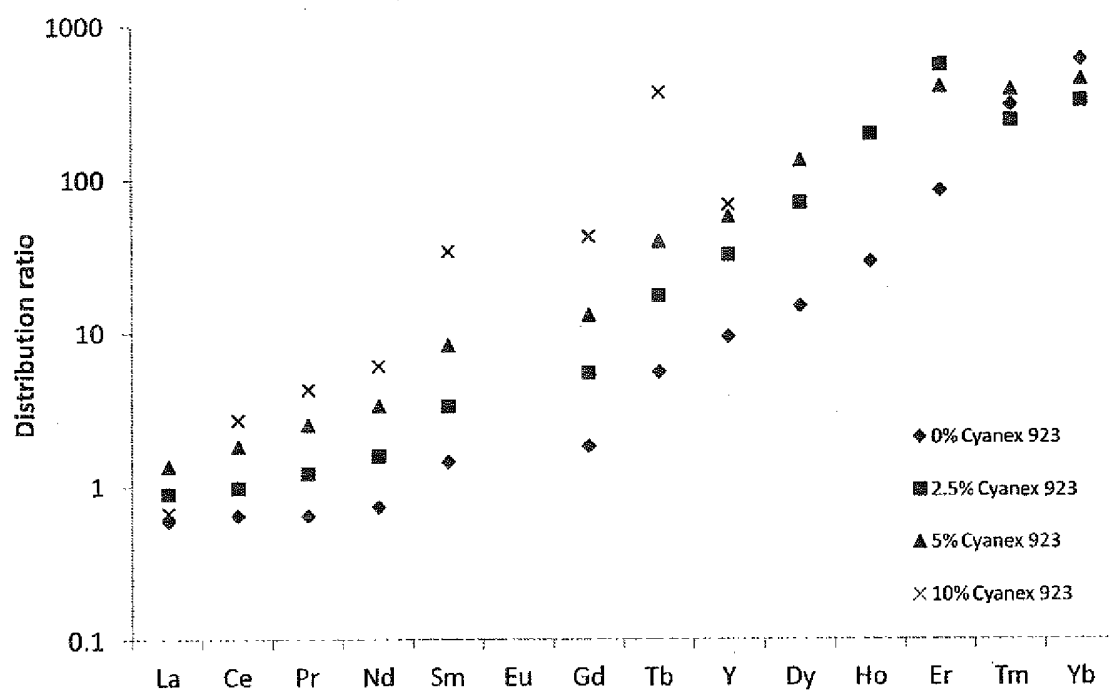


Figure 7.

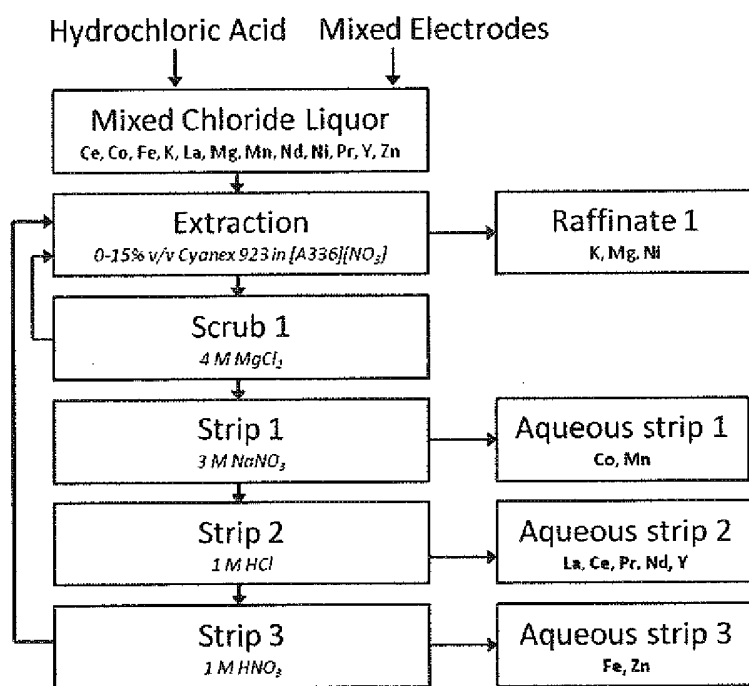


Figure 8.

# INTERNATIONAL SEARCH REPORT

International application No

PCT/BE2015/000003

## A. CLASSIFICATION OF SUBJECT MATTER

INV. B01D11/04 C01F17/00 C22B3/00 C22B9/00 C22B59/00  
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

B01D C01F C22B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EP0-Internal, WPI Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 751 553 A (GAUDERNACK B ET AL) 7 August 1973 (1973-08-07) examples 1-7	1-6,8, 12-24
X	----- LILI ZHU ET AL: "The preparation of supported ionic liquids (SILs) and their application in rare metals separation", SCIENCE CHINA CHEMISTRY, SP SCIENCE CHINA PRESS, HEIDELBERG, vol. 55, no. 8, 25 June 2012 (2012-06-25), pages 1479-1487, XP035095876, ISSN: 1869-1870, DOI: 10.1007/S11426-012-4632-8 paragraph [2.1.2] ----- -/--	1,5,7, 9-12,24



Further documents are listed in the continuation of Box C.



See patent family annex.

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Date of the actual completion of the international search

22 April 2015

Date of mailing of the international search report

19/05/2015

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# INTERNATIONAL SEARCH REPORT

International application No

PCT/BE2015/000003

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>XIAOQI SUN ET AL: "The solid-liquid extraction of yttrium from rare earths by solvent (ionic liquid) impregnated resin coupled with complexing method", SEPARATION AND PURIFICATION TECHNOLOGY, vol. 63, no. 1, 8 July 2011 (2011-07-08), pages 61-68, XP055180836, ISSN: 1383-5866, DOI: 10.1016/j.seppur.2008.03.038 the whole document</p> <p>-----</p>	1-24

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/BE2015/000003

Patent document cited in search report	Publication date	Patent family member(s)	Publication date	
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			FR 2214660 A1	19-08-1974
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